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Vol. VII

TRANSCRIPT OF RECORD

PATENT EXHIBITS

Supreme Court of the United States

OCTOBER TERM, 1930

No. 378

STANDARD OIL COMPANY (INDIANA), STANDARD OIL COMPANY (NEW JERSEY), STANDARD DEVELOPMENT COMPANY, ET AL., APPELLANTS,

vs.

THE UNITED STATES OF AMERICA

APPEAL FROM THE DISTRICT COURT OF THE UNITED STATES FOR THE NORTHERN DISTRICT OF ILLINOIS

FILED AUGUST 23, 1930

(35,300)

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SUPREME COURT OF THE UNITED STATES

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APPEAL FROM THE DISTRICT COURT OF THE UNITED STATES FOR THE NORTHERN DISTRICT OF ILLINOIS

VOL. VII

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107—Treatise on petroleum	791	4010
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129—Russian patent No. 12,926	961	4208
130—German patent No. 166,723	966	4213
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136—French patent No. 322,265	1008	4268
137—French patent No. 399,722	1016	4277
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139—French patent No. 390,558	1037	4299
140—British patent No. 27,005	1048	4310
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150—Letters patent No. 342,564	1116	4404
151—Excerpt from Chemiker Zeitung, 1895.	1120	4410
152—Excerpt from Engler-Hofer-Das Erdol, Vol. 1	1122	4411
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154—Excerpt from Chemiker Zeitung, 1896.	1127	4416

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156—French patent No. 343,390	1131	4419
157—French patent No. 108,214	1136	4424
158—Excerpt from Dingler's Polytechnische Journal, 1878	1140	4428
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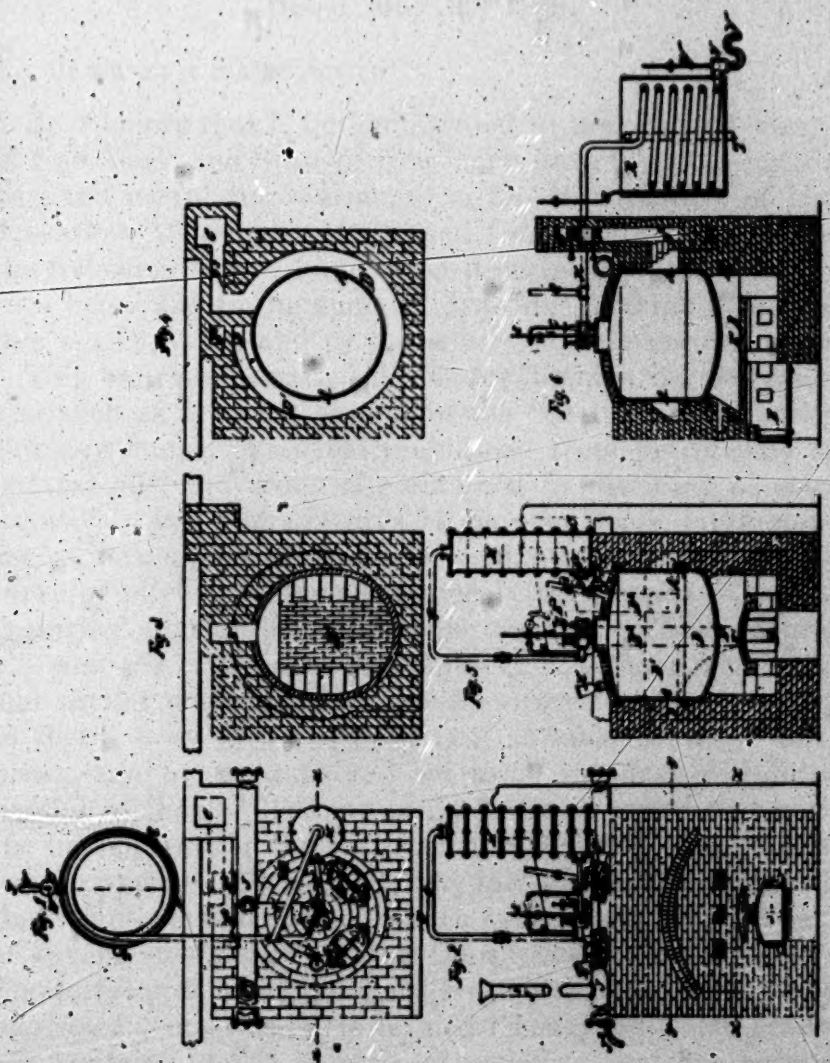
[fol. 693]

PETITIONER'S EXHIBIT 80

L. ATWOOD.

Oil Still.

No. 28,448. Patented May 29, 1860.



Witnesses.

PX 80-1

Inventor.

[fol. 694] United States Patent Office

Luther Atwood, of New York, N. Y.

Improvement in the Manufacture of Oils Obtained from Coal

Specification Forming Part of Letters Patent No. 28,448, Dated May 29, 1860

To all whom it may concern:

Be it known that I, Luther Atwood, of the city and county of New York, and State of New York, have invented certain new and useful Improvements in the Manufacture of Hydrocarbon Illuminating-Oils; and I do hereby declare that the following is a full and exact description thereof, reference being had to the annexed drawings, making a part of this specification, and to the letters of reference thereon.

Thin hydrocarbon oils suitable for illuminating purposes, and such as are now burned in the "Deitz," and similar chimney lamps, are usually obtained from petroleums or natural oils, and crude oils obtained by distilling at comparatively low temperatures bituminous coals, bituminous shales, bituminous schists, peat asphaltums, rosin, and the tarry or pitchy residue remaining in the process of manufacturing adamantine or stearine candles. These natural oils and the crude oils, distillates of the above-mentioned and similar substances, it has heretofore been the practice to distill over in a cast-iron still suitable for such purposes, and to separate and set aside the first or lighter portion of the distillate, or such portion as comes over until the temperature in the still rises to about 600° Fahrenheit, for the purpose of manufacturing into illuminating-oil, with the exception, sometimes, of such exceedingly volatile part as can be steamed off during the process of manufacture. The latter portion of the distillate, which comes over at an increased temperature, is termed "heavy oil." It generally contains visible crystals of paraffine, and has heretofore been generally manufactured into lubricating-oils and candles. By repeated simple distillations of the heavy oil a further quantity of thin oil has been obtained, the heavy

oil remaining containing larger proportionate quantities of paraffine. I mention this in order that it may not be confounded with my process.

My said invention consists in a method of treating these heavy oils, paraffine, fatty oils and acids, or the crude oils and natural oils from which the heavy oils are produced, as above mentioned, so that the whole or as much as desired may be converted into thin oil suitable, when purified, to burn in lamps.

My process is a practical development, embodiment, and combination of two operations peculiar to these bodies in a process of continuous distillation—viz: first, a gradual and continuous application of sufficient heat to the substance acted on to initiate chemical changes which result in the decomposition or breaking up of the heavy bodies and the formation of light and heavy oil-vapors, and comparatively small amount of fixed gases accompanied with deposition of carbon in the still; second, a continuous separation of the light thin oil-vapors and fixed gases from the heavier oil-vapors, and continuous condensation and return of the latter to the sphere of action of the heat until the whole is broken up, or nearly so, or as much as desired, by exposing the eliminated vapors in a chamber or receiver of considerable capacity situate between the point of forming the vapor and the condenser to a temperature about the boiling-point of the lighter vapors and below the boiling-point of the heavier vapors, so that the heavy vapors gradually liquefy and return to be broken up by further action of the heat, while the desired light product passes over to the condenser, where it is liquefied and separated from the fixed gases.

It will be observed that, owing to the fact of the return to the action of the heat of the heavy oil when it is nearly at the boiling-point, a comparatively small increase of temperature is necessary to break it up. This gives my process a great economical advantage over the former practice of successive plain redistillations, by which a further portion of thin oil has heretofore been obtained from heavy oils, as described in the beginning of this specification.

The apparatus I prefer to use is figured in the annexed drawings, of which Figure No. 1 is a plan view; Fig. No. 2,

a front elevation; Fig. No. 3, horizontal section through dotted line *x x*, Fig. No. 2; Fig. No. 4, horizontal section through dotted line *y y*, Fig. No. 2; Fig. No. 5, transverse section through dotted line *x x*. Fig. No. 1; No. 6, vertical longitudinal section through dotted line *y y*, Fig. No. 1.

Letter A represents a cast-iron still constructed with a removable lower section for the purpose of convenient repair. The bottom of the still is heated by products of com- [fol. 695] bustion supplied to the chamber B from the — box E, the arch E′, with its piers and passages, serving to divide and distribute the products of combustion equally within the chamber B. B′ is a short horizontal passage connecting the chamber B with the flue B^2, which is furnished with a damper, B^3, and connects with the chimney C.

D is an uptake opening out of the passage B and leading up to the flue D′, which, passing around the sides of the still, connects with the chimney C by the passage D^2, which is furnished with a damper, D^3. When the damper B^3 is closed and the damper D^3 open, the products of combustion from the chamber B are forced to pass through the flue D′, heating the sides of the still on their way to the chimney. I use the flue D′ in this manner in commencing a distillation. After the distillation has commenced, I shut the damper D^3 and open the damper B^3 in the passage B^2, which connects the chamber B directly with the chimney.

Letters F F are two man-holes for removal of residue, provided with the covers and fastenings.

Letter G is a filling-pipe provided with a stop-cock, (shown broken off,) but must be connected with a reservoir of unfinished oil.

Letter H is a funnel-pipe provided with a stop-cock, used also for filling the still.

Letter I is a weighted safety-valve on the dome of the still, through which vapors can escape when, from any cause, the worm becomes choked. The stem of the valve is fitted to receive a slotted weight, and terminates in a ring-handle, by which it may be raised up and hooked on the hook I′ when necessary to keep the passage open.

Letter J is a main or condensing pipe, connected with the safety-valve by the blow-off pipe J′. The condensable products escaping through the safety-valve and saved in the main J flow out through the small pipe J^2 into any suitable

receiver, the fixed gases and vapors not condensed escaping through the discharge-pipe J*, (shown broken off,) but to be carried up through the roof of the building, or in any suitable manner away from the vicinity of the still.

Letter K is a pipe connecting the worm-condenser with the still through the angle-valve L.

Letter M represents a vertical cast-iron chamber of cylindrical form, standing on the top of the brick-work casing of the still and near the still. This chamber I call a "separating" chamber. It connects with the still by the superior pipe N through the angle-valve O, also by the inferior pipe P, which is furnished with a stop cock. The pipe Q, provided with a stop-cock, connects the top part of the separating-chamber with the worm-condenser through the pipe K. The separator is made in sections connected by flanges and screw-bolts for the purpose of conveniently increasing or diminishing its capacity. The worm-condenser is situated in a water-tub, R, supplied with cool water from a force-pump or a reservoir, by the inflow-pipe S, the surplus flowing out through the pipe T. The worm terminates in a small chamber, U, from the bottom of which the liquid products escape through the sealed siphon-pipe V, the fixed gases passing up through the gas-pipe W, (shown broken off,) but to be carried up through the roof or away from the vicinity of the still. The gas-pipe W is furnished with a stop-cock, to be closed when necessary, to blow steam through the chamber U and siphon V for the purpose of removing obstructions or to cleanse them.

Letters *a*, *b*, and *c* are steam-pipes, each provided with a suitable valve or stop-cock, connecting, respectively, with the dome of the still, the pipe K, and the pipe N, and by a branch coupling with a steam-pipe, *d* (shown broken off,) but which must be connected with a steamboiler.

Letter *e* is a draw-cock used for the purpose of discharging condensed steam from the steam-pipe.

The steam-pipe *a* is used in combination with the safety-valve outlet when open, the other openings in the still being closed for the purpose of expelling by pressure of steam the vapors and gases remaining in the still at the completion of a distillation, and also after removal of the residue, to prepare the still, when hot, for the safe reception of a charge of oil by forcing steam into the still in sufficient quantity to

displace atmospheric air, as described in other Letters Patent of the United States to me.

When the angle-valve L is shut and the stop-cock in the pipe Q, which connects the separating-chamber with the pipe K, is closed, steam may be blown through the worm-condenser from the steam-pipe *b*, for the purpose of removing obstructions and cleansing the condenser. When the angle-valve O is shut and the stop-cock closed in pipe P and the pipe Q open, steam may be blown through the separating-chamber and condenser from the steam-pipe C.

For the purpose of the process herein described, the direct connection from the still to the worm-condenser through the angle-valve L is kept closed, to be opened when desirable to interrupt the process of obtaining light thin oil from heavy oil, and to run over heavy oil. In that case the connections to and from the separating-chamber are to be closed.

The operation of my process is as follows: The apparatus having been arranged for the operation as above described, I place the substance to be acted on in the still and gradually and continuously apply sufficient heat externally to initiate chemical changes, which results in breaking up or decomposing the substance acted on, forming light and heavy oil-vapors, with comparatively small quantity of permanent gases, and with accompanying deposition of carbon in the [fol. 696] still. The vapors and gases pass through the superior pipe N upward into the separating-chamber M. The separating-chamber being exposed externally to the cooling influence of the atmosphere of the still-room, and heated only by the radiated heat from the top of the still and the incoming vapors and gases, a temperature comparatively higher or lower in proportion to the relative quantity of incoming vapor, but sufficiently below the boiling-point of the major portion of the heavier or higher boiling-point vapors to gradually liquefy them is maintained internally, and as they liquefy and fall to the bottom of the separating-chamber they are continuously returned to the still through the inferior pipe P. The lighter vapors and permanent gases gradually rise to the top of the separator and pass on through the pipe Q to the worm-condenser, the liquid products passing out at V, the gases escaping upward through the pipe W.

From the above description it will be evident to those skilled in the art that the particular character of the distillate will depend on the degree of rapidity with which the

operation is conducted within such limits as it can be carried on at all in the above-described apparatus. If vapors are not formed with sufficient rapidity and in sufficient quantity to keep the internal temperature of the separator up to a point about the boiling-point of the lighter vapors, they will, of course, all condense and fall back in the still. If heat is applied so actively as to form vapors rapidly enough to keep the temperature nearly up to about the boiling-point of the heavy vapors, a portion of them will be forced over and condensed with the lighter vapors. Therefore the particular degree of change resulting from any one operation will be governed by the relative quantity and degree of heat applied.

It is not material in the practical working of my process to effect the desired change in one operation, neither is it generally convenient or practical to do so; but within the limits above mentioned the slower the operation is conducted the greater will be the change effected by one distillation.

During the necessary and commonly practiced processes of purifying hydrocarbon illuminating-oils by treating them repeatedly with acids and caustic alkalies, they are subjected to redistillation, which may be performed by my process, and the operation of converting heavy oil into light oil go on with the purification process, with which it does not interfere.

When carrying on my process in this manner, after the purification is completed I prefer to distill over such portion of the purified oil as will go over at below about 600° Fahrenheit, with the still arranged so as to have direct communication with the condenser through the angle-valve L, and with the separating-chamber cut off. This portion is then fit for use. The remaining contents of the — are then run over through the separator, — for reasons not necessary to mention here, being obvious to those skilled in the art, subjected to further treatment.

When crude oil is subjected directly to my process the light portion, generated simultaneously with the heavy bodies in the original production of the crude oil by distilling coal or other substances, passes over until the temperature of the still rises above about 600° Fahrenheit, when my process of breaking up the heavy bodies commences. The

relative height of the separating-chamber is an important element in its proportion, because it favors separation of the vapor by difference of specific gravity.

The proportion, situation, and arrangement of the separating-chamber as figured in the drawings I consider best for a still such as shown with a body or boiler of about seven feet in diameter. In a still of such dimensions I carry on the operation at the rate of ten gallons per hour.

Although I prefer the apparatus herein described and figured, and consider it best adapted to carry on my process rapidly and profitably, I will nevertheless use any form of apparatus or still in which I can practically carry on my process.

The illuminating-oils resulting from my process, when purified and finished as usual — illuminating-oils heretofore manufactur- from the lighter parts of the crude oils, do not differ materially from them in color or mobility; but owing, perhaps, to the greater proportionate quantity of paraffine in the source from which they are immediately derived, they possess greater illuminating-power. In the practical manufacture of these oils they may be beneficially mixed with other light oils; or when operating on crude oil the distillate of both light and heavy parts may be suffered to run into the same cistern or other receiver.

By the use of my process above described the manufacturer can, by a comparatively small number of distillations, break up or convert the whole heavy liquid and solid portions of the crude oil into light thin illuminating-oil whenever it is desirable to do so.

What I claim as my invention and improvement in the manufacture of hydrocarbon illuminating-oils is—

The production of thin oils suitable to be manufactured into illuminating-oils from the heavier parts of the crude and fixed oils and other substances within mentioned by treating them in manner substantially as hereinbefore described during one or several continuous distillations.

Luther Atwood.

Witnesses: Braind. G. Latimer, F. C. Treadwell, Jr.

3906

[fol. 697]

PETITIONER'S EXHIBIT 81

(No Model.) 4 Sheets—Sheet 1.

N. M. HENDERSON

APPARATUS FOR DISTILLING OR REFINING MINERAL OILS.

No. 340,878. Patented Apr. 27, 1886.

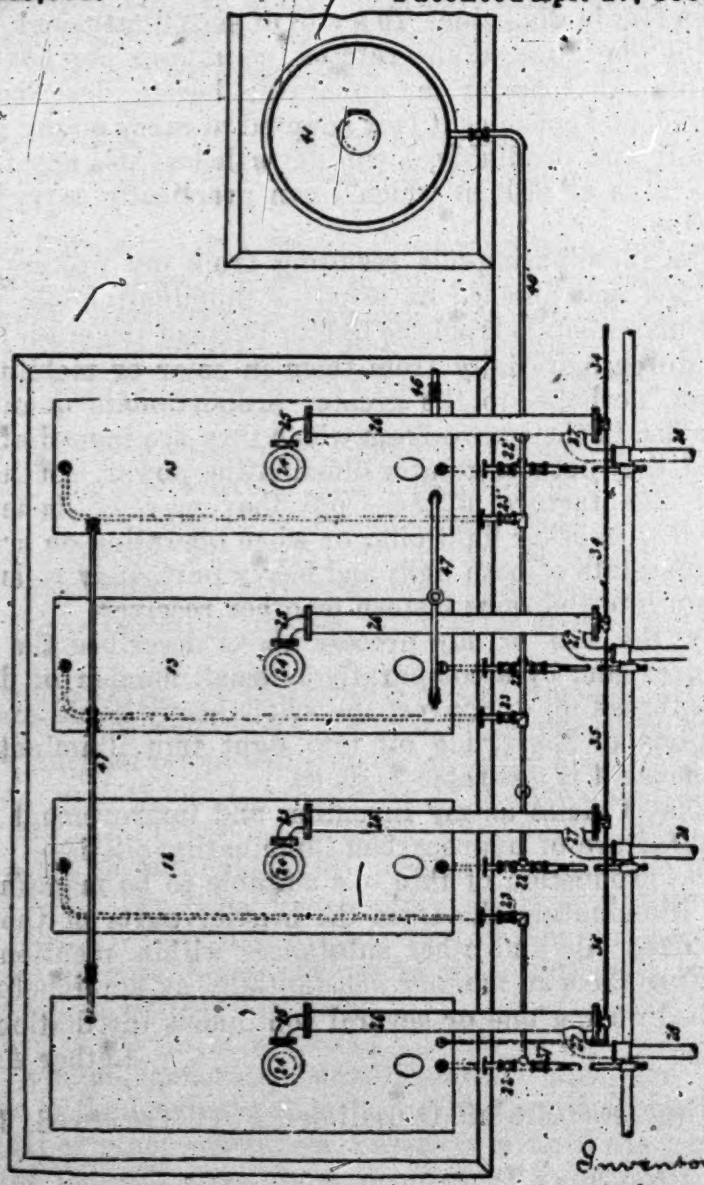


FIG. 1.

Witnesses:
Wm. Reasser
John E. Parker
Harry Burgess

PX 81-1

Inventor:
N. M. Henderson
by his Attorneys
Howson and Howson

[fol. 698]

(No Model.) 4 Sheets—Sheet 2.

N. M. HENDERSON.

APPARATUS FOR DISTILLING OR REFINING MINERAL OILS.

No. 340,878. Patented Apr. 27, 1886.

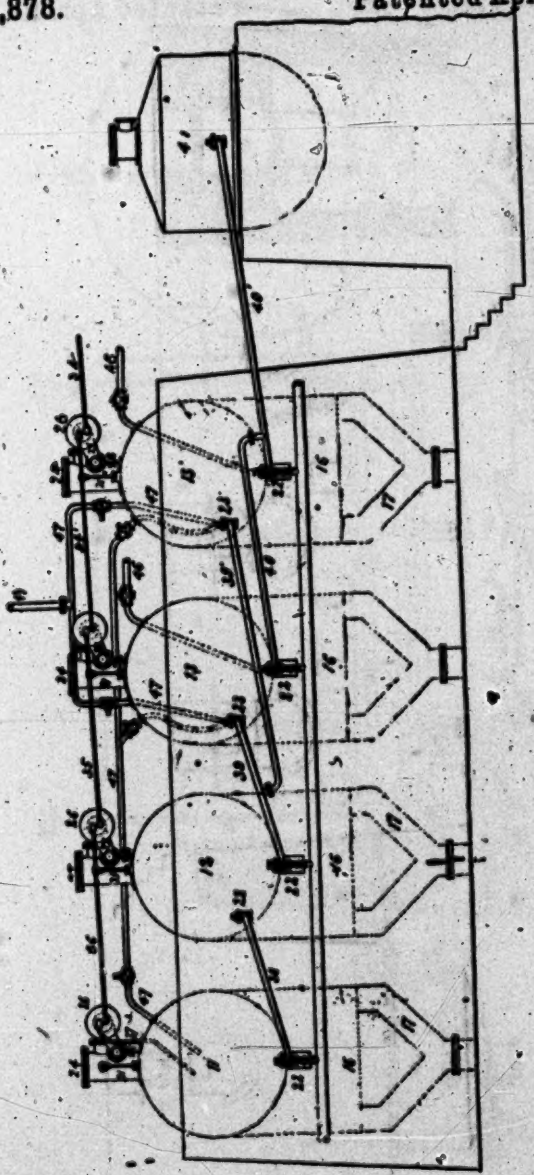


FIG. 2

Witnesses:
John C. Tarran
Barry Davis

Inventor:
N. M. Henderson
by his Attorneys
Howson and Sons

3908

[fol. 699]

(No Model.) 4 Sheets—Sheet 3.

N. M. HENDERSON.

APPARATUS FOR DISTILLING OR REFINING MINERAL OILS.

No. 340,878. Patented Apr. 27, 1886.

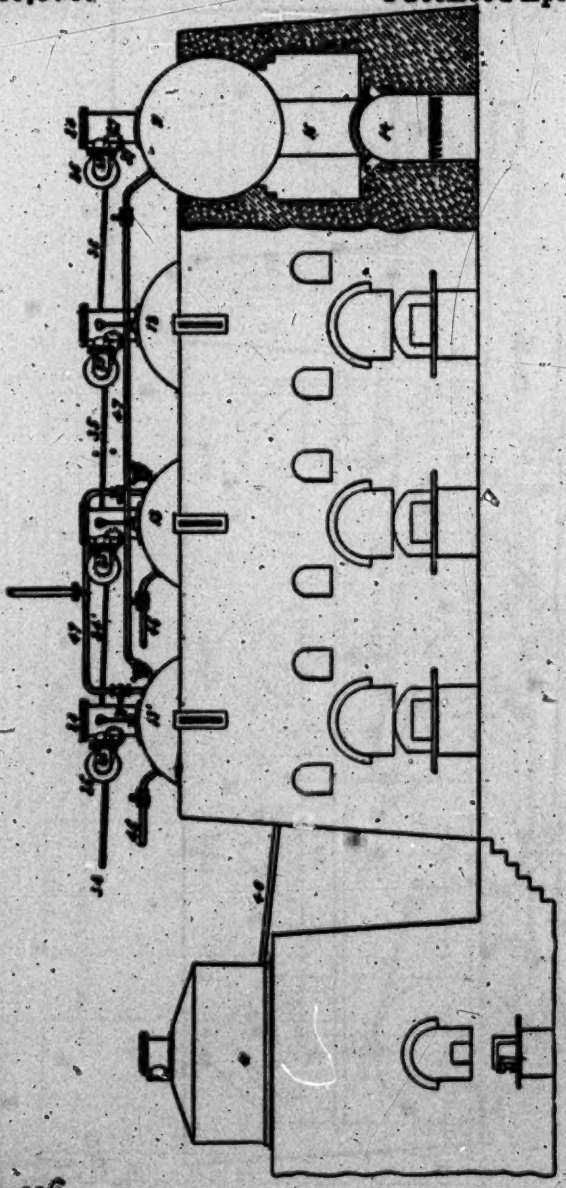


FIG 3

Witnesses:
John C. Pavar
Harry Drury

PX 81-3

Inventor:
N. M. Henderson
by his Attys
Norton and Bros

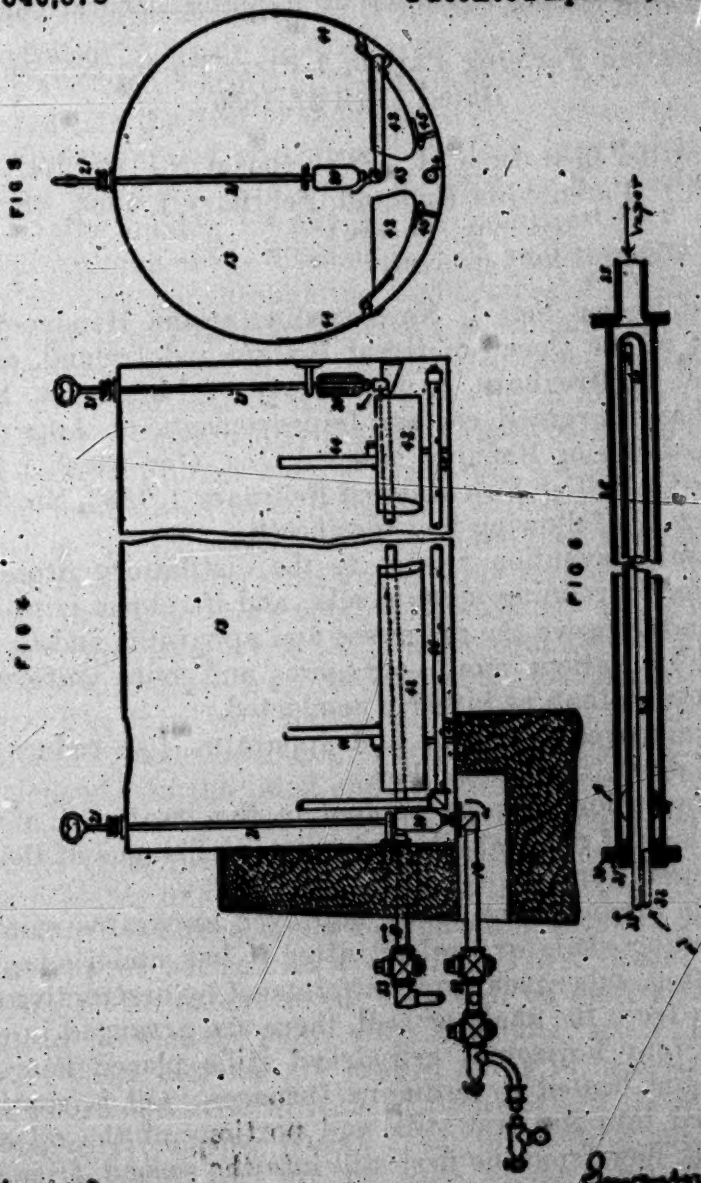
[fol. 700]

(No Model.) 4 Sheets—Sheet 4.

N. M. HENDERSON.

APPARATUS FOR DISTILLING OR REFINING MINERAL OILS.

No. 340,878 Patented Apr. 27, 1886.



Witnesses
John E. Power
Henry Dewey

FIG. 4

Inventor
N. M. Henderson
by his Attorneys
Howson and Sons

[fol. 701] United States Patent Office

Norman M. Henderson, of Broxburn, County of Linlithgow, Scotland

Apparatus for Distilling or Refining Mineral Oils

Specification Forming Part of Letters Patent No. 340,878, Dated April 27, 1886

Application filed June 11, 1885. Serial No. 168,344. (No model.) Patented in England, February 1, 1883, No. 540

To all whom it may concern:

Be it known that I, Norman Macfarlane Henderson, a subject of the Queen of Great Britain and Ireland, and a resident of Broxburn, in the county of Linlithgow, Scotland, have invented certain Improvements in Apparatus for Distilling or Refining Mineral Oils, (for which I have obtained a British Patent dated February 1, 1883, No. 540,) of which the following is a specification.

My said invention relates to the distillatory processes employed in refining mineral oils; and its object is to simplify and improve the processes and apparatus and to render the operations more continuous and more uniform in their results than as hitherto conducted.

My improved processes and apparatus also reduce the cost of plant, fuel, and labor.

My invention may be applied in the treatment of various kinds of mineral oils and at various stages of the refining operations.

In one arrangement of my improved apparatus suitable for treating shale or coal oil after it has undergone one distillation, subsequent to its attainment by destructive distillation from the shale or coal, there are arranged in connection four horizontal cylindrical stills placed near together and heated by ordinary furnaces. Oil is continuously fed into the first still, and portions of the oil continuously flow from the first still into the second, from the second into either the third or fourth, and from the third or fourth into one or more residue-stills, and in each still the inlet is kept as far separated as possible from the out-

let leading to the next still. The inlets are also placed at higher levels than the outlets, and both inlets and outlets are provided with special safety-valves hereinafter particularly described. Each still is formed with the usual dome or vapor-chest, into which the volatilized oil rises, and from which it passes by a curved branch into a long horizontal cylinder or pipe, wherein its heat is utilized in raising the temperature of the oil which is being continuously fed into the first of the three stills. These feed-heating cylinders are of special construction, hereinafter particularly described, and which is such as to render impossible the mixing of any of the comparatively crude feed-oil with the newly-distilled oil. The oil supplied to the first still is passed through the feed-heaters of all the three stills, and the distillation proceeds continuously, the temperature maintained in the second still being higher than in the first, and that in the third or fourth higher than in the second. Consequently the oils vaporized in the several stills are of different specific gravities; but the oil vaporized in or distilled over from each still is always of one quality or specific gravity so long as the feed and the heats applied to the several stills are suitably regulated. In each still the lighter or more volatile constituents of the oil rise and are vaporized, while the heavier constituents draw to the bottom, and are transferred thence, to the next still in order. The third and fourth stills are both for the third distillatory stage, one being in action while the other is being cleaned. In the third and fourth stills, where there is a tendency for coke or adhesive carbonaceous matter to separate from the oil, there are fitted inside of the stills certain plates or dishes, to promote the circulation of the oil, and to form receptacles for the coke, so that it may not adhere to the bottoms of the stills. These dishes or circulating-plates extend along each still on each side of its longitudinal central plane with a middle space between them. Their bottoms are shaped so as to be nearly parallel to or concentric with the bottom shell of the still, and the oil in circulating passes from the middle under the dishes or plates and up the sides of the still, returning downward from the sides toward the middle, and this circulation is assisted and insured by jets of steam issuing from perforations in the sides of a pipe extending along

the still near the middle of the bottom. If found necessary or desirable, the circulating plates or dishes may be applied to the second still, and even to the first. Two or more residue-stills are, by preference, provided in connection with each set of three connected stills, in order that while one of the residue-stills is being cleaned out there may be no interruption in the continuous action of the three stills.

Instead of heating the oil supplied to the first still by means of the vapor-feed heaters, as hereinbefore described, [fol. 702] or in addition to that means of heating, it may be heated by being passed through a coil of piping in the third still; or the feed-oil may be heated in any other convenient way.

Figure 1 on Sheet 1 of the accompanying drawings is a plan, and Fig. 2 on Sheet 2 is a back-elevation, of a set of four stills with one of the residue-stills. Fig. 3 on Sheet 3 is a front elevation partly in section. Figs. 4 and 5 on Sheet 4 are enlarged longitudinal and transverse vertical sections representing the third and fourth stills, and Fig. 6 is an enlarged longitudinal section of one of the feed-heaters. In these drawings the same reference-numerals are used to mark the same or like parts wherever they are repeated.

In the arrangement shown in the drawings there are four horizontal cylindrical stills, 11 12 13 13′, placed near together in a suitable building and heated by ordinary furnaces, 14, a convenient size for these stills being seven feet in diameter by about nineteen feet in length. The fire-place of each furnace, or the space immediately over the grate, is arched over, and the fire-gases pass through lateral openings 15, Fig. 3 into a heating chamber, 16, in which they act directly on the still, and from one end of which they pass off downward by lateral flues 17 (indicated by dotted lines in Fig. 2) to a main underground flue leading to the chimney.

Each still is fitted with an outlet or discharge pipe, 18, in the bottom at one end, and in the second, third, and fourth stills, 12 13 13′, an inlet-pipe, 19, enters the same end at a higher level, but is continued inside the still to the other end, so that the actual inlet may be as far as possible from the outlet. The orifices inside the stills of both the inlet and outlet pipes 19 18 open or face upward, and plug-valves 20 are provided within the stills for closing them when

necessary, these valves 20 consisting of conical loaded valves attached to vertical rods 21, which pass out through stuffing-boxes in the tops of the stills and are ordinarily held up by any simple appliance which can be disconnected at a moment's notice to allow the valves to close. Thus in the event of the external stop-cocks, 22 23, or any pipe connections or joints getting out of order the safety-valves 20 can be instantly closed, so as to prevent leakage of the oil.

Each still is formed with the usual dome or vapor-chest, 24, into which the volatilized oil rises, and from which it passes by a curved branch, 25, into a long, horizontal cylinder or pipe, 26, wherein its heat is utilized in raising the temperature of the oil which is being continuously fed into the first, 11, of the stills.

As shown in Fig. 6, each feed-heating cylinder 26 is a cylindrical pipe with flanged ends, with an inlet, 25, at one end for the vapor, and with an outlet, 27, for the same at the side near the other end, this outlet 27 being in a curved branch communicating with the pipe 28, which leads the vapor to the condenser. Within the outer pipe, 26, there is fixed an inner pipe, 29, the inner end of which is closed, while its outer end is formed with or has tightly fixed to it by screwing, a flange, — by means of which a tight joint is formed with the flange at the outlet end of the outer pipe, 26. The outer end of the inner pipe, 29, is closed by a plate, 31, which has fixed through it a short pipe, 32, extending only a short distance inward, and a longer pipe, 33, which extends almost to the inner end, and the feed oil is admitted by the shorter pipe 32, and passes off by the longer one 33, after being subjected to the heating action of the vapor passing between the outer cylindrical pipe, 26, and the inner one, 29. The feed-oil passes through the heaters 26 of all the stills, being led from one to the other through pipes 34 34′ 35 36, and finally passing by a pipe, 37, into the first still, 11, the pipe dipping a short distance below the surface of the oil in that still. While the distillation is proceeding continuously in the stills 11, 12, 13, or 13′, there is a continuous transference of oil from the first still, 11, to the second still, 12, by a pipe, 38, connecting the outlet-pipe 18 of the first still to the inlet-pipe 19 of the second still. Similarly, there is a continuous transference of oil from the second still, 12, by a pipe, 39 or 39′, either to the third still, 13, or to

the fourth still, 13′, and from the third or fourth still, 13 or 13′, by a pipe, 40 or 40′, to one or more residue-stills, 41. As the specific gravity of the oil varies in the stills 11, 12, 13 or 13′, the surface-levels of the oil will be — correspondingly different levels. When operating upon an average quality of shale-oil with stills of the size shown in the drawings—that is, of seven feet diameter, I believe the best working-levels are five feet, four and one-half feet, and four feet, respectively, in the stills 11, 12, 13, or 13′. As there is a tendency for coke or carbonaceous adhesive matter to separate in the third still, 13, a fourth still, 13′, and connections are provided to allow of either still 13 or 13′ being cleaned, thus enabling the apparatus to work without interruption. If the still 13 is in use, the stopcocks 22′ 23′ are closed, and the oil is transferred through the pipes 40 40′ to the residue-stills 41; but when the still 13′ is in use the stop-cocks 22 23 are closed and the stop-cocks 22′ 23′ opened, the oil being then transferred directly from the still 12 through the pipe 39′ to the still 13′, from which it passes through the stop-cock 22′ and pipe 40′ to the residue-still 41.

The residue-still 41 is at a lower level than the other stills, and the stop-cocks on the pipes 40 40′, leading to it, are in practice to be adjusted to allow of such a flow from either of the third-stage stills 13 or 13′ as will cause the levels mentioned to be maintained without much variation. The heats applied to the several stills must also be regulated to suit the different qualities or specific gravities of oil which is found is practice to be most advantageously volatilized in each still. It will, however, be obvious to [fol. 703] those conversant with the refining of mineral oils that the rates of feed and of flow of the oil through the stills, the levels in the several stills, and the heats applied will in practice have to be adjusted to suit the particular oil operated upon in each case.

The dishes or plates 42, for promoting circulation and for colecting coke, and which will in general be applied to the third and fourth stills, 13 13′, are shown in Figs. 4 and 5 on Sheet 4. There are two dishes, 42, in each still, each being made with a curved bottom nearly concentric with the bottom of the still, while there are vertical ends and a

nearly-vertical side along the inner part of each, there being a middle space, 43, between the two dishes. The dishes 42 are jointed to straps or hinges 44, riveted to the sides of the still, and are supported by feet 45, rings or shackles being jointed to them for the attachment of chains by which the dishes can be turned up for cleaning purposes. At the lower part of the middle space, 43, between the dishes 42, there is a longitudinal steam-pipe, 46, which has perforations made along the lower part of each side. The oil in circulating passes down the middle space, 43, between the dishes 42, and being aided by the steam-jets from the pipe 46, passes under the dishes 42 and up the sides of the still, the non-volatilized portions returning downward above the dishes 42 and toward the middle space, 43. As the circulating currents are at their slowest while passing over the dishes 42, the coke which separates from the oil tends to be deposited in the dishes instead of on the bottom of the still, and it can be removed from the dishes periodically.

As hereinbefore mentioned, the oil fed or supplied to the first still, 11, or some of that oil, instead of being heated by the feed-heaters 26 may be heated by passing through a pipe, 47, led through the third or fourth stills, 13 or 13′, in which still it is arranged in a number of lengths or coils. On leaving the third or fourth still, 13 or 13′, the pipe 47 is represented as passing directly to the first still, 11; but it might also be led through the second still, 12, if found desirable.

What I claim as my invention is—

1. The combination of the still and its inlet and outlet pipes, having the usual stop-cocks outside the still, with weighted valves 20, applied to the said pipes within the still, and having handles extending to the outside, all substantially as specified.

2. In combination with the set of three connected stills working at graduated temperatures, the feed-heaters consisting each of an outer pipe, through which the vapor from the still is passed, and which has within it a pipe having a closed inner end and fixed by its outer end, through which outer end inlet and outlet pipes for the feed-oil are inserted, substantially as hereinbefore described.

3. The dishes or plates 42, arranged to promote circulation in the still, and also to receive the coke, the said dishes being hinged at their outer sides, and having a space between each and the bottom of the still and also a central longitudinal space between the two dishes, substantially as and for the purposes hereinbefore described.

4. The combination of the still with dishes or plates therein to receive the coke, and having a longitudinal space between them, and a perforated steam-pipe to promote circulation around said dishes, substantially as set forth.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

N. M. Henderson.

Witnesses: Edmund Hunt, David Ferguson.

[fol. 704] PETITIONER'S EXHIBIT 93

British Patent No. 3345, A. D. 1865

Specification in Pursuance of the Conditions of the Letters Patent Filed by the said James Young in the Great Seal Patent Office on the 26th June 1866

To all to whom these presents shall come, I, James Young, Junior, of Limefield, in the County of Mid Lothian, North Britain, Gentleman, send Greeting.

Whereas Her most Excellent Majesty Queen Victoria, by Her Letters Patent, bearing date the 27th day of December, in the year of our Lord One thousand eight hundred and sixty-five, in the 29th year of Her reign, did, for Herself, Her heirs and successors, give and grant unto me, the said James Young, junior, Her special license that I, the said James Young, junior, my executors, administrators, and assigns, or such others as I, the said James Young, junior, my executors, administrators, or assigns, should at any time agree with, and no others, from time to time and at all times thereafter during the term therein expressed, should and lawfully might make, use, exercise, and vend, within the United Kingdom of Great Britain and Ireland, the Channel

Islands, and Isle of Man, an Invention for "Improvements in Treating Hydrocarbon Oils," upon the condition (amongst others) that I, the said James Young, junior, my executors or administrators, by an instrument in writing under my hand and seal, should particularly describe and ascertain the nature of the said Invention, and in what manner the same was to be performed, and cause the same to be filed in the Great Seal Patent Office within six calendar months next and immediately after the date of the said Letters Patent.

Now Know Ye, that I, the said James Young, junior, do hereby declare the nature of my said Invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement, that is to say:

This Invention relates to the treatment of certain hydrocarbon oils, such as those obtained from the distillation of coal or shale at a comparatively low temperature, and known as paraffin oils, or such as petroleum, either crude or more or less refined, with a view to the reduction of the specific gravity of such oils, and otherwise to the beneficial alteration of their properties. In the preparation of these oils it is desirable for commercial purposes that the proportion of heavy oils to the lighter or burning oils should be as small as possible on account of the greater demand [fol. 705] for burning oils, but in the processes hitherto employed the production of heavy oils has been unavoidably large, to the great detriment of the manufacturer.

My invention applies both to the heavy and light oils, rendering both lighter and improving their quality, but its importance is greater as applied to the heavy oils.

In carrying out my Invention I take the hydrocarbon oil to be operated upon and run it into any convenient boiler or distilling vessel, which to ensure safety should be made of sufficient strength to resist a pressure of at least one hundred pounds to the square inch, the heat being applied thereto in the usual manner. The oil contained therein is thereby converted into vapour, which may be allowed to pass to the condenser under any desired pressure, and such pressure may be regulated by means of a valve loaded to the extent of pressure required. The compressed vapour or volatile product of distillation may be allowed either to

pass through such valve or through a separate tube with regulating stop cock to the refrigeratory or condensing apparatus, where the products are collected in the usual manner. An ordinary steam pressure guage may be employed for the purpose of indicating the pressure. The result of my process is that a large proportion of the oils originally operated upon are converted into oils of lower specific gravity. I have found in practice that a pressure of about twenty pounds to the square inch in the boiler or vapour generating vessel is suitable for the treatment of heavy hydrocarbon oils obtained from coal or shale, but such pressure may be varied to some extent. The apparatus employed may be of various forms, but I have found that an ordinary steam boiler, not tubular, answers the purpose efficiently; the more capable it is of being easily cleaned the better, as the heavy deposits should be removed therefrom at intervals, such deposit, if allowed to remain, seriously interfering with the process of distillation. The vaporization or distillation under pressure may also be applied to the before-mentioned hydrocarbon oils in various stages of rectification; for instance, the crude oil or first product of distillation may be at once treated, or the crude oil may be first distilled in the usual manner, and the products of such redistillation may be treated according to my Invention; or the of distillation may be separated into two portions, and the heavier portions may be treated according to my Invention, but it will be all cases that the result of my process is to convert the hydro- inwhatever state they are operated upon into

(Last 4 lines unreadable.)

oils of a ligther nature. I do not claim any particular form [fol. 706] of apparatus employed, but what I claim is, the distillation of paraffin oils and petroleum under pressure, thus obtaining improved products therefrom.

In witness whereof, I, the said James Young, junior, have hereunto set my hand and seal, this Twenty-fifth day of June, One thousand eight hundred and sixty-six.

James Young, Junior. (L. S.)

London: Printed by George Edward Eyre and William Spottiswoode, Printers to the Queen's most Excellent Majesty. 1866.

PETITIONER'S EXHIBIT No. 94

Proceedings of the Royal Society of London From June 16, 1870, to June 15, 1871

Vol. XIX

50.968

(Filed U. S. Patent Office, May 23, 1885)

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MDCCCLXXI

(Pages 370-371)

II. "Preliminary Notice on the Production of the Olefines from Paraffin by Distillation under Pressure." By T. E. Thorpe, Ph. D., Professor of Chemistry in Anderson's University, Glasgow, and John Young. Communicated by Professor Roscoe, F. R. S. Received February 2, 1871.

When paraffin is exposed to a high temperature in a closed vessel, it is almost completely resolved, with the evolution of but little gas, into hydrocarbons which remain liquid at the ordinary temperature.

This reaction will undoubtedly afford the most important insight into the constitution of this body.

Accordingly we have repeated this conversion on a large scale, and from about 3½ kilograms of paraffin melting at 44°·5C. (prepared from shale) we have obtained nearly [fol. 707] four litres of liquid hydrocarbons. This mixture of hydrocarbons commences to boil at about 18° C., but the quantity coming over below 100° C. is comparativley small; by far the greater portion boils between 200° and 300°. A preliminary separation shows that the four litres are made up of hydrocarbons boiling

	Litres
Between 200° and 300°	2·7
" 100° and 200°	1·0
Below 100°	0·3
	4·0

Up to the present we have principally occupied ourselves with the investigation of the fraction boiling below 100°, and have obtained conclusive evidence that it is mainly composed of olefines, the proportion of members of the $C_n H_{2n}$ +2 series being but small. By repeated fractionations over sodium we obtained perfectly colourless liquids boiling about 35° and 65°, which were attacked by bromine in the cold with the greatest energy. On adding the bromine slowly and in minute drops, and carefully cooling the hydrocarbon by a mixture of snow and salt, scarcely a trace of hydrobromic acid was produced. The portion boiling at 36° may be either amylhydride or amylene, or a mixture of both; the avidity with which the bromine combines with it shows that the latter body must be present in considerable quantity. As soon as the drops of bromine permanently coloured the liquid, it was submitted to distillation. Only a small portion came over below 40°; the thermometer rose rapidly to 180°, and nearly the whole of the bromine-compound distilled at 184° to 188°. This substance is amylene bromide, $C_5 H_{10} Br_2$; Wurtz gives the boiling-point of this body at about 180°. The portion therefore boiling at 35° is mainly amylene.

Exactly similar results were obtained from the portion boiling at 65° to 70°. This, from its boiling point may be either $C_6 H_{12}$ or $C_6 H_{14}$, or a mixture of both. Bromine disappears instantly on adding it to the carefully cooled liquid, and on distillation by far the greater portion is found to have combined with the halogen. The bromine thus obtained distils with slight decomposition about 195°. Pelouze and Cahours found that hexylene bromide, $C_6 H_{12} Br_2$, boiled at 192° to 198°.

We are at present engaged in the further investigation of this subject, and hope shortly to lay our results before the Royal Society.

[fol. 708] PETITIONER'S EXHIBIT No. 95.

Proceedings of the Royal Society of London from November 16, 1871, to June 20, 1872

(Filed U. S. Patent Office May 22, 1885)

Vol. XX

50. 969

London:

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MDCCCLXXII

(Pages 488 to 491)

XVIII. "On the Combined Action of Heat and Pressure upon the Paraffins." By T. E. Thorpe and John Young, of the Andersonion University, Glasgow. Communicated by Prof. Roscoe, F. R. S. Received June 5, 1872

(Abstract).

The authors first refer to their preliminary communication read before the Royal Society on March 9, 1871, in which they described the combined effect of heat and pressure upon the solid paraffins. They showed that when these substances are exposed to a high temperature in a closed vessel, they are almost completely resolved, with the evolution of but little gas, into hydrocarbons which remain liquid at the ordinary temperature. In the present communication they describe how this transformation may be easily effected on the small scale. A few grams of ordinary paraffin are sealed up in a piece of strong combustion-tubing, bent in the form of the letter V; the tube is securely surrounded by strong wire gauze, and the limb containing the paraffin is gently heated along its entire length in a gas combustion-furnace. If the heat is properly regulated, the paraffin rapidly distils over and solidifies in the cold [fol. 709] portion of the tube. The gas-flames are then

turned down, the tube reversed, and the paraffin again distilled. After a few repetitions of this process the paraffin acquires the consistency of butter, and the warmth of the hand is sufficient to liquefy it; and after about a dozen distillations, the greater portion of the substance remains permanently liquid. It seems to be absolutely necessary that the paraffin should thus be distilled over and condensed; by merely heating it in the tube in such a manner that the condensed vapours flow back again upon the heated portion, the liquefaction is never accomplished. It appears that only paraffins boiling at an extremely high temperature, and those usually solid under ordinary conditions, are thus susceptible of decomposition. The readiness with which they yield liquid hydrocarbons appears to depend upon the complexity of their constitution.

The authors have not determined with certainty the limits of the decomposition, but they find that the mixed paraffin and olefine, boiling at about 255°, may be repeatedly distilled backwards and forwards in a sealed V-tube without suffering the slightest change.

The authors have repeated the process of conversion of solid paraffin into liquid products upon a large scale, in the hope of obtaining an insight into the constitution of the higher members of the $C_n H_{2n} + 2$ series of hydrocarbons. The paraffin employed was obtained from shale; it melted at 46°, and had a specific gravity (when solidified under pressure) of 0.906 at 13°. Its composition was:

Carbon	84·14
Hydrogen	14·81
	99·95

The apparatus employed is fully described in the original memoir. 3½ kilograms of paraffin yielded about 4 litres of liquid made up of hydrocarbons boiling

	Litres
Below 100°	0·3
From 100-200°	1·0
From 200-300°	2·7
	4·0

A considerable quantity of substance which could not be distilled within the range of the mercurial thermometer re- [fol. 710] mained in the retort, and solidified on cooling. By repeated recrystallization from ether, this substance was obtained of a constant melting-point (41°·5). Its composition was:

Carbon	85·19
Hydrogen	15·34
	100·53

The action of bromine upon this body showed that it was a member of the $C_n H_{2n} + 2$ series. Heated in a sealed tube in the manner above described, it was readily split up into liquid hydrocarbons, which were shown to be mixtures of hydrides and olefines.

The four litres of liquid were submitted to a systematic fractional distillation over sodium; the greater portion of the operation was effected in an apparatus after Warren's design. The following fractions were thus isolated (boiling-points uncorrected):

		°	°		
(1)	at	35-	37	(7) at	193-195
(2)		65-	70	(8)	212-215
(3)		94-	97	(9)	230-235
(4)		122-	125	(10)	252-255
(5)		145-	148	(11)	273-276
(6)		170-	172	(12)	290-295

By means of bromine all these fractions were shown to be mixtures of hydrides and olefines; and an attempt was made in each to determine, by means of this reagent, the relative quantities of the two series of hydrocarbons. The method by which this was accomplished is detailed in the original memoir. It was shown that in the lower fractions (up to 200°) the amount of hydride was sensibly equal to that of the olefine. Thus the fraction boiling at 65-70° was shown to be a mixture of hexane and hexylene in equal proportions; the fraction at 94-97° was also made up of heptane and heptylene in equivalent amounts. In the higher fractions, however, there is a decided increase in the amount of the hydride present.

After the treatment with bromine the hydrides could be isolated in the pure state. The authors obtained:

[fol. 711]	Boiling-point	Sp. gr.
	° °	
Pentane	37	
Hexane	67- 68	0·6631 at 18 C.
Heptane	97- 99	0·6913 " 18·5
Octane	122-125	0·7165 " 15·6
Nonane	147-148	0·7279 " 3·5

From their specific gravities and boiling-points these hydrides in all probability belong to the series of normal paraffins.

$$CH_3—CH_2\ldots\ldots\ldots\ldots\ldots\ldots(nCH_2)—CH_3$$

The authors have established the existence of the olefines not only by the action of bromine, but also by the preparation of a number of brominated derivatives. They have obtained:

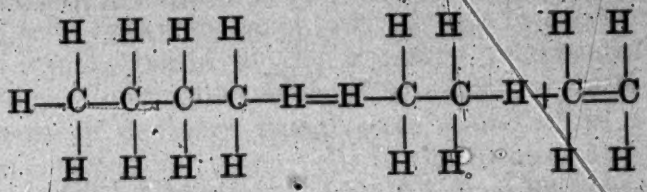
	Boiling-point	Sp. gr.
	° °	
$C_5H_{10}Br_2$	184-188	
$C_6H_{12}Br_2$	195-200	1·5967 at 20
$C_7H_{14}Br_2$	decomposes	1·5146 at 18·5
$C_8H_{15}Br$	185-190	
$C_8H_{16}Cl_2$	about 235° with decomposition.	
C_9H_{17} Br	208-212	

They have also prepared a few derivatives from the hydrides, and studied the action of nitrogen tetroxide upon the mixture boiling at 122-125°.

The mode of decomposition of the paraffins under the influence of heat and pressure appears to be general for the higher terms of the series of normal hydrocarbons.

If the paraffins be represented constitutionally, by linking together the carbon atoms in a single chain, the simultaneous formation of hydride and olefine obviously arises from the loosening of the affinities of the CH_2 groups. Under the influence of heat, these groups became disassociated, and recombine to form saturated hydrocarbons. Assuming, for the sake of simplicity, that this decomposition may occur so low

down in the series as in the case of butane, it might be thus represented:—



[fol. 712] The authors have but little direct evidence to offer as to the exact manner of this decomposition—whether it is attended by the gradual elimination of ethylene, a hydride containing a greater number of carbon atoms being left behind, or whether the paraffin is at once split up into hydride and olefine containing an equal number of carbon atoms as in the above equation. Neither supposition is exactly substantiated by experiment. If the action of heat gave rise to the former mode of decomposition, we ought to obtain a larger quantity of ethylene after prolonged heating, especially when the liquefied portion is rich in hydrocarbons of low molecular weight; but it has already been pointed out that the process of liquefaction is accompanied with the production of comparatively little gas. On the other hand, an examination of the amounts of bromine required to render the hydrocarbons boiling above 200° permanently red, shows that the proportion of hydride to olefine in the several mixtures becomes gradually larger as the molecular weight increases.

It would doubless have been interesting to have determined the relative amounts of the twelve fractions isolated from the decomposed paraffin; but when it is considered that their separation was only effected after several thousand distillations, it will be evident that the quantities obtained after such prolonged treatment can afford no real indication of the amounts present in the original liquid. It appears, however, that the amounts of liquid boiling at 94-97° and 122-125° were but slightly, if at all, less than the quantities boiling at 252-255° and 273-276°.

[fol. 713] PETITIONER'S EXHIBIT No. 96

Proceedings of the Royal Society of London from November 21, 1872, to November 27, 1873

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MDCCCLXXIII

(Pages 184 to 200)

Transactions (continued).

Vienna:—Anthropologische Gesellschaft. Mittheilungen. Band II. nr. 3-5, 7, 8. 8vo. Wien 1872. The Society.

Adams (John R.) Dulwich College and the Endowed Schools Commissioners. A Tract for the Times. 8vo. London 1873. The Author.

Dumas (J. B.), For. Mem. R. S. Éloge Historique de Isidore Geoffroy Saint-Hilaire. 4to. Paris 1872. The Author.

Rogers (H. D.) The Geology of Pennsylvania, a Government Survey, with a General View of the Geology of the United State. 2 vols. in 3, and volume of Maps. 4to. Edinburgh 1858. Professor Huxley, Sec. R.S.

Topsöe (H.) og C. Christiansen. Krystallografisk-optiske Undersögelser, med særligt Hensyn til isomorfe Stoffer. 4to. Kjöbenhavn 1873. The Authors.

[fol. 714] "On the Combined Action of Heat and Pressure upon the Paraffins." By T. E. Thorpe and John Young, of the Andersonian University, Glasgow, Communicated by Prof H. E. Roscoe, F.R.S. Received June 5, 1872*.

1. In a preliminary communication read before the Royal Society on March 9th, 1871†, we described the combined ef-

* Read June 20, 1872. See abstract, vol. xx. p. 488.

† Proc. Roy. Soc. vol. xix. p. 370.

fect of heat and pressure upon the solid paraffins. We showed that when these substances are exposed to a high temperature in a closed vessel they are almost completely resolved, with the evolution of but little gas, into hydrocarbons which remain liquid at the ordinary temperature. This transformation may be easily effected on the small scale. A few grms. of ordinary paraffin are sealed up in a piece of strong combustion-tubing bent in the form of the letter V: the tube is securely surrounded by stout wire gauze, and the limb containing the paraffin is gently heated along its entire length in a gas combustion-furnace. If the heat is properly regulated, the paraffin rapidly distils over and solidifies in the cold portion of the tube. The gas-flames are then turned down, the tube reversed, and the paraffin again distilled. After a very few repetitions of this process the paraffin acquires the consistency of butter, and the warmth of the hand is sufficient to liquefy it, and after about a dozen distillations it remains permanently liquid. Although there is no difficulty in thus ultimately effecting the resolution of the solid paraffin into liquid products, the rapidity of the transformation seems to be dependent upon conditions which we cannot yet say we have satisfactorily determined. On one occasion, after all the paraffin had been distilled over and had solidified in the colder limb of the tube, the empty portion in contact with the flame became softened and blew out, when instantly, on the removal of the pressure, the solid matter became liquid, and slightly effervesced as if gas had been condensed in the substance by the pressure to which it had been subjected. It seems to be absolutely necessary that the paraffin should be thus distilled over and condensed; by merely heating it in the tube in such a manner that the condensed vapours flow back again upon the heated portion, the liquefaction of the paraffin is never accomplished. About 6 grms. of a pure paraffin, melting at 41°·5 C. (see section 12), were heated in a sealed tube to about 200° for twelve hours, [fol.715] but the melting-point remained unchanged. The same portion of paraffin was then transferred to a V-tube surrounded by wire gauze, and distilled backwards and forwards in the combustion-furnace. After six distillations it was rendered completely liquid. The total quantity of liquid obtained was about 6 cub. centims. On gently warming it, bubbles of gas were evolved, and the liquid was in full ebullition at 40°, but only about one sixth came over below 100°;

about 2½ cub. centims. distilled between 100° and 200°, and nearly the whole of the remainder below 300°; the small quantity remaining solidified when the bulb was plunged into cold water.

2. It appears that only paraffins boiling at an extremely high temperature, and those usually solid under ordinary conditions, are thus susceptible of decomposition. The readiness with which they yield liquid hydrocarbons appears to depend upon the complexity of their constitution. We have not determined with certainty the limits of the decomposition; but we find that the paraffin (and olefine) boiling at about 255° (see section 11) may be repeatedly distilled backwards and forwards in a sealed V-tube without suffering the slightest change. 6-7 grms. of the mixture of hydrocarbons were distilled backwards and forwards twenty-one times; but on opening the tube no gas was evolved, and the boiling-point (252°-255° uncorrected) remained unaltered. A further proof of its unalterability on repeated distillation under pressure is afforded by its reaction with bromine (see section 5).

I. 9·38 grms. of the mixed hydrocarbons before distillation required 2·95 grms. of bromine before the liquid became permanently reddened; 100 parts by weight would require 31·4.

II. 8·605 grms. hydrocarbon before distillation required 2·672 grms. of bromine, or 100 grms. would require 31 of bromine. Mean amount of bromine needed 31·2 per cent.

III. 5·13 grms. of the hydrocarbon after repeated distillation (21 times) required 1·54 grms. of bromine, or 100 grms. would require 30 grms.

3. In the hope of throwing some light upon the constitution of the solid paraffins, we have repeated this process of transformation into liquid products upon a large scale. The paraffin employed was obtained from shale; it melted at 46° and solidified at 43°, and had a specific gravity of 0·906 at 13°, when solidified under an extra pressure of [fol. 716] 0·75 millim. of mercury*.

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* Considerable discordances exist in the statements by various observers of the specific gravities of the solid paraffins. These differences are doubless due more to the dif-

It was burnt with copper oxide in a stream of oxygen, with the following results:

I. 0·2980 grm. paraffin gave 0·9293 grm. carbon dioxide and 0·3980 grm. water.

II. An unknown quantity gave 1·4245 grm. carbon dioxide and 0·6060 grm. water.

	I	II	Mean
Carbon	85·05	85·23	85·14
Hydrogen	14·84	14·77	14·81
	99·89	100·00	99·95

---

ficulty of obtaining the bodies perfectly homogenous after melting than to any great variations in their true specific gravity. When a piece of ordinary paraffin is examined, it is seen to be made up of an infinite number of small cavities; and however carefully it may be cooled after melting, the interstices are invariably present. From this circumstance it is obvious that any attempt to determine the real specific gravity of this body would give too low a result. By solidifying the paraffin under pressure, the formation of the cavities may be, to a great extent, obviated. We have effected the solidification in the apparatus figured in the margin. Mercury was first poured into the tube up to the level A B, the bottom end of the tube being securely plugged by a cork C. The wider portion D of the tube was then filled with the melted paraffin, and a well-fitting caoutchouc cork fastened down by wire into the opening, care being taken to exclude all bubbles of air. Mercury was now quickly poured into the longer limb of the tube until it stood about 0·8 m. above the level of the metal in the wider tube, and under the pressure of this mercury the paraffin was allowed to solidify slowly. By withdrawing the cork C, the mercury could flow out, and on warming the sides of the tube the plug of paraffin was easily detached. Thus solidified, the body was almost entirely free from cavities, and portions perfectly homogeneous were easily found; these had a specific gravity of 0·906 at 13°.

(Cut unproducible)

[fol. 717] These numbers agree perfectly with those obtained by Anderson many years ago* from analysis of a paraffin identical in origin and melting-point (45°·5) with that employed by us. Dr. Anderson found for the substance the composition:

Carbon	85·1
Hydrogen	15·1
	102·2

A sample of paraffin from peat, melting at 46°·7, gave:

	I	II	Mean
Carbon	84·95	85·23	85·09
Hydrogen	15·05	15·16	15·10
	100·00	100·39	100·19

In the process of conversion we replaced the bent glass tube above described by an apparatus consisting of two cast-iron mercury bottles connected together by a bent iron pipe, in which were fixed a stopcock and pressure-gauge. One of the bottles was charged with the paraffin, and was heated over an ordinary coal fire, the heat being so regulated that a pressure of 20 to 25 lbs. was maintained in the apparatus throughout the operation. The volatilized products distilled over into the second bottle, which acted as a condenser. In about four or five hours the operation was concluded, and the distillate had the appearance of a magma of oil, and of apparently unaltered paraffin. This mixture melted at a comparatively low temperature, the warmth of the hand being sufficient to render it completely liquid.

Three and a half kilograms of the paraffin yielded about 4 litres of liquid hydrocarbons. On distillation the mixture commenced to boil at 18°, but the quantity coming over below 100° was comparatively small; by far the greater portion boiled between 200° and 300°. A preliminary

* Rep. Brit. Assoc. 1846.

separation showed that the 4 litres were approximately made up of hydrocarbons boiling:

	Litres
I. Below 100°	0·3
II. From 100-200°	1·0
III. From 200-300°	2·7
	4·0

[fol. 718] A considerable quantity of substance, which could not be distilled within the range of the mercurial thermometer, remained in the retort, and solidified on cooling (see section 12). Each of the portions was then submitted to a systematic fractional distillation.

4. Fraction boiling below 100°.—After repeated distillations over sodium this portion was almost completely resolved into three fractions, boiling constantly at (1) 32-38°, (2) 65-70°, and (3) 94-97°. The quantity of liquid boiling below 30° did not amount to 5 cub. centims. Although the distillation was conducted in winter, and freezing-mixtures of snow and salt were employed for the condensation, the greater portion of the product boiling at 32-38° came over at about 35°; this boiling-point would indicate that the liquid is probably either quintane or amylene, or a mixture of these hydrocarbons. In order to decide the point, the distillate was treated with bromine. The liquid was violently attacked, and each drop of bromine combined with the hydrocarbon with a hissing noise; so energetic was the reaction, that, in order to moderate it, it was necessary to immerse the hydrocarbon in a freezing-mixture. When proper care was taken to cool the liquid, scarcely a trace of hydrobromic acid was evolved. In order to prevent the possible formation of higher brominated products, the addition of the bromine was from time to time interrupted, and the liquid submitted to distillation; it invariably commenced to boil at about 32°, and the distillation was maintained until the thermometer stood at 50°. The distillate was again treated with bromine in the cold, and again distilled, the process being repeated until it was without visible action upon the hydrocarbon,—that is, until the liquid was permanently reddened. It was then washed

with dilute potash solution, and rectified over sodium; it boiled constantly at 35-37°; the liquid was evidently quintane, and in all probability normal quintane, the boiling-point of which is given by Schorlemmer at 37-39°, and by Warren at 37°. The amount was far too small to attempt the preparation of any derivatives from it. The brominated portion boiling above 50° was then distilled; the thermometer rose rapidly to 180°, and the whole of the liquid came over below 200°. After renewed distillation the liquid was found to boil constantly, but with slight decomposition at 184-188°; this compound is amylene dibro- [fol. 719] mide, the boiling-point of which, according to Wurtz is in the neighborhood of 180°.

0·6515 grm. bromide gave 1·0125 grm. Ag Br and 0·235 grm. reduced silver.

	Calculated	Found
Br	69·5	68·8

5 The fraction boiling between 65° and 70°, which was at least fifty times greater than that boiling at 32-38°, was then treated with bromine; the bromine was absorbed with the same avidity as in the preceding case; and it was equally necessary to cool the hydrocarbon in order to moderate the reaction As soon as the liquid appeared permanently reddened, it was distilled. The portion boiling below 80° was no longer instantly attacked by bromine; it was accordingly free from the accompanying olefine. The distillate was then treated with aqueous potash to remove the free bromine, and when colourless the hydrocarbon was decanted, dried, and distilled over sodium; it boiled almost entirely between 65° and 70°, by far the greater portion coming over at 67-68°. It was analyzed with the following results:

0·1440 grm. hydrocarbon gave 0·2095 grm. water; the carbon determination was lost.

	Calculated	Found
C_6	83·72	——
H_{14}	16·28	16·16
	100·00	

Two determinations of its specific gravity made by means of different bottles gave:

(1) 0·6620 at 19°·5, and
(2) 0·6641 at 18°.

Compared with water at the same temperature, Pelouze and Cahours found 0·669 at 16° for the hexane boiling at 68° obtained from American petroleum. Hexane from suberic acid, boiling at 69°·5, according to Dale, has a specific gravity of 0·6617 at 17°·5; this agrees with that of *B* hexane obtained from mannite, viz. 0·6645 at 16°·5. Schorlemmer found 0·678 at 15°.5 for the hydride from cannel coal, which agrees perfectly with that obtained by Williams for the same hydride prepared from boghead coal, viz. 0·6745 at 18°. On the other hand, Schorlemmer has found that the hexane prepared from mannite is probably identical with [fol. 720] that obtained for secondary hexyl iodide by the action of zinc and hydrochloric acid, and with the dipropyl obtained from primary hexyl iodide, for which he found the specific gravity 0·6630 at 17°; and these are probably identical with the hexane of Pelouze and Cahours obtained from petroleum, and with the hydride found by Schorlemmer in cannel oil, all being normal hydrocarbons with the constitution

$$CH_3—CH_2—CH_2—CH_2—CH_2—CH_3$$

The brominated hydrocarbon left in the flask after removing the hexane was then distilled: it commenced to boil at about 190°; the thermometer gradually rose to 195°, and nearly the whole of the liquid distilled over below 205°. As the compound showed signs of decomposition on boiling, hydrobromic acid being continuously evolved during the distillation, a considerable amount of tarry matter remaining in the flask, it was impossible to fractionate it further. It was purified, however, by distillation in a current of steam; it was nearly colourless, and on analysis yielded numbers agreeing with the formula $C_6H_{12}Br_2$.

0·8950 grm. of the bromide gave 1·3570 grm. silver bromide and 0·0090 grm. reduced silver.

	Calculated	Found
Br	65·57	65·28

The following are the data obtained in the determination of its specific gravity:

Weight of bottle	1·6807 grm.
Bottle + water at 20°	7·2942 grms.
Bottle + bromide at 20°	10·6440 "

from which 1.5967 is obtained as the specific gravity of hexylene dibromide at 20° compared with water at the same temperature.

A second determination with a smaller quantity gave 1·5975 at 18°. Pelouze and Cahours found the boiling-point of this body to be 192-198°, and its specific gravity 1·582 at 19°. These numbers are certainly too low; the bromide had probably been slightly decomposed by distillation.

We have attempted to determine the relative amounts of hydride and olefine in the fraction boiling at 65-68° by means of the reaction with bromine.

The hydrocarbon was weighed out in a small distillation-flash, and well cooled by a mixture of ice and salt; bromine [fol. 721] was then slowly added, and in minute drops, by means of the little apparatus seen in the figure—a small caoutchouc ball about .5 cub. centims. in diameter, which can be compressed by the plate movable along the rods by means of the milled head-screw. The mode of working the instrument is obvious; by means of it the bromine can be easily transferred from the bottle in which it is preserved to the hydrocarbon, and the amount added can be regulated with great nicety. The bromine was added until the liquid was permanently reddened, when the flask was again weighed to determine the amount of bromine employed. 13·30 grms. of the mixed hydrocarbons boiling at 65-70° required 13·16 grms. bromine before the red colour was persistent. This amount of bromine is equivalent to 6·9 grms. of hexylene, and 13·3 — 6·9 = 6·4 as the amount of hexane present. The mixture was now distilled, and all passing over below 110° (at which point the liquid in the flask commenced to blacken) collected in a weighed test-tube. The weight of the distillate was 6·18 grms. From these numbers it would appear that the product boiling at 65-68° is a mixture of hexane and hexylene in about equal proportions.

6. The fraction boiling at 94-97° was next treated with bromine in the cold until the liquid was reddened. The termination of the reaction was not so easily seen in this case; the mixture blackened slightly, and more hydrobromic acid was evolved, although the hydrocarbon was carefully cooled by ice and salt. The brominated mixture on distillation commenced to boil about 95°, and it was heated to 130°, when the liquid in the flask commenced to decompose; at this point, therefore, the distillation was interrupted. The following are the details of a quantitative determination:

Weight of mixed hydrocarbons	14·21	grms.
Weight of bromine added	12·9	"
Equivalent to heptylene	7·9	"
Equivalent to heptane	6·3	"
Amount of heptane actually obtained	6·15	"

From this experiment it would appear that the amount of olefine is slightly greater than that of the hydride in the fraction boiling at 94-97°; but, from the circumstances of the experiment, we have reason to believe that the amount of heptylene thus indicated is slightly above the truth. It was difficult to determine the final point of the reaction; the hydride was not altogether unacted on by the bromine, and [fol. 722] small quantities of hydrobromic acid were continuously disengaged during the process; these circumstances would tend to increase the weight of bromine used, and consequently the apparent weight of the olefine present. In extending our research to the determination of the constitution of these hydrocarbons, we have had occasion to repeat this experiment on a far larger scale and under more favourable conditions.

900 grms. of the mixed heptane and heptylene required 716 grms. of bromine; this would be equivalent to 439 grms. of heptylene. 900 grms. of a mixture of heptane and heptylene in equivalent proportions would contain 444 grms. of heptylene.

The heptylene bromide could not be redistilled under the ordinary atmospheric pressure without decomposition; it commenced to blacken at about 150°, and dense fumes of hydrobromic acid were evolved. When distilled in a current of steam, it was obtained nearly colourless.

It cannot be preserved, however, without slight decomposition; when exposed to light, it slowly darkens in colour and evolves hydrobromic acid gas.

It was analyzed with the following results:

0·7470 grm. gave 1·0210 grm. Ag. Br and 0·035 grm. reduced silver.

	Calculated for $C_7H_{14}Br_2$	Found
Br.	62·01	61·66

The specific gravity of this compound was found to be 1·5146 at 18°·5, water at the same temperature being taken as unity.

The heptane, after washing with dilute potash solution, drying, and rectification over sodium, boiled constantly at 97-99°. Its specific gravity was found from two experiments to be (1) 0·6910 at 19°, and (2) 0·6915 at 18°. Warren and Storer found for the same hydrocarbon from Menhadden oil the specific gravity of 0·6942 at 1°·5.

Burnt with copper oxide in a stream of oxygen, it yielded the following numbers:

I. 0·1695 grm. hydride gave 0·5240 grm. carbon dioxide and 0·2460 grm. water.

II. 0·2638 grm. hydride gave 0·8119 grm. carbon dioxide and 0·3733 grm. water.

III. An unknown quantity gave 0·5015 grm. carbon dioxide and 0·2318 grm. water.

[fol. 723]

	Calculated	Found I	Found II	Found III
C_7	84·00	84·29	83·94	84·14
H_{16}	16·00	16·13	15·73	15·86
	100·00	100·42	99·67	100·00

These six bodies, quintane and amylene, hexane and hexylene, heptane and heptylene, are the only liquids we have been able to isolate from the fraction boiling below 100°. Careful search was made for the other hydrocarbons, particularly for benzol and for the hexylene of Cav-

entou, boiling about 80°, but without success. The fractions intermediate between 70° and 90° could be resolved by repeated distillations into products boiling at 65-70° and 90-100°. The amount coming over in the neighbourhood of 80° was very small; in fact the entire quantity eventually obtained between 70° and 90° amounted to only a few grams. About a gram of the small portion boiling at 80-82° was treated with strong nitric acid; the liquid was very slowly acted upon, and when treated with alcohol, zinc, and hydrochloric acid, after washing and solution in ether, it failed to give the characteristic reaction for aniline; nor on treating the remainder of the hydrocarbon with excess of bromine, and allowing the mixture to evaporate, could any solid promide ($C_6 H_{10} Br_4$) be obtained. Hence we infer the absence of members of the $C_n H_{2n-2}$ and $C_n H_{2n-6}$ groups in the liquid hydrocarbons obtained by the decomposition of solid paraffins.

7. Fraction boiling between 100° and 200°.—As this portion amounted to about a litre, it was thought worth while to attempt a more rigorous separation of the hydrocarbons than is possible by the ordinary method of fractionation; for this purpose a small condensing arrangement on Warren's principle was constructed, and by means of it the hydrocarbons were separated at first at intervals of 10°, afterwards into portions boiling between 5°, and eventually into portions boiling between 2°. The hydrocarbons were distilled over sodium, and the temperature of the worm was maintained about 20° lower than that of the vapour in the flask. A considerable quantity of liquid was obtained boiling below 100°; and this could be resolved into hexane and hexylene, heptane and heptylene. The amount of liquid eventually obtained between 100° and 120° was very small.

About 120 grms. of liquid were found to boil constantly [fol. 724] between 122° and 125°. Bromine was eagerly absorbed by this fraction, indicating the probable presence of octylene, the boiling-point of which is given by Bouis at 125°, and by Pelouze and Cahours at 118-120°. The reaction with bromine yielded the following data:

Amount of hydrocarbon taken	41·0 grms.
Amount of bromine needed	34·0 "
Equivalent of octylene	24·1 "

On addition of bromine the hydrocarbon darkened rapidly in colour, and a small quantity of tarry matter collected at the bottom of the flask. As it was impossible to distil the mixture under the ordinary atmospheric pressure, the bromide being decomposed by a very slight elevation of temperature, it was treated with alcoholic potash, and distilled per ascensum for some hours until a few drops thrown into water floated upon its surface. Water was then added, the lighted portion separated, dried, and fractionated. The largest amount came over between 120° and 140°, the next fraction from 140-160° being much smaller in quantity, whilst scarcely any liquid distilled over between 160° and 180°. After this point the thermometer became more stationary, and a fraction almost as large as that at 120-140° came over between 180° and 200°. This, on renewed distillation, boiled at 185-190°; it had a feeble garlic smell, and was heavier than water. Analysis showed that it had approximately the composition $C_8 H_{15} Br$.

I. 0·4755 grm. bromide gave 0·4165 grm. silver bromide and ·0180 grm. reduced silver.

II. 0·4600 grm. bromide gave 0·4100 grm. silver bromide and 0·0150 grm. reduced silver.

		Found	
	Calculated	I	II
Br	41·8	40·1	40·7

According to Rubien*, by whom this compound was first described, its boiling-point is 185°

The fraction boiling between 120° and 140° on repeated distillation was separated into octane, boiling at 122-125°, and a liquid of an alliaceous odour boiling constantly at 130-135°, which absorbed bromine with avidity. This in all probability was caprylidene, the boiling-point of which has already been found by Rubien (loc. cit.) to be 133-134°; [fol. 725] its formation was doubtless due to the prolonged action of the alcoholic potash on the $C_8 H_{15} Br$.

Action of chlorine on mixed hydrocarbons boiling at 122-125°.—34 grms. of the hydrocarbons were weighed out into

*Ann. Ch. Pharm., vol. cxiii, p. 294.

a small distillation-flash, immersed in a mixture of ice and salt, and a gentle stream of chlorine sent through the liquid in the dark. The chlorine was rapidly absorbed, and for the first hour but little hydrochloric acid was disengaged; during the second hour and to the close of the operation, the evolution of this gas increased largely, and the mixture darkened considerably.

The chlorinated liquid was then distilled in a current of steam; as soon as the distillate appeared to be heavier than water the receiver was changed, and the heavy liquid separated, dried, and distilled. It commenced to boil at about 220°, but showed no constant boiling-point; but the greater portion came over between 230° and 240°. At this high temperature the product suffered rapid decomposition. The portion boiling at 230-240° was redistilled in a current of steam. After drying over calcium chloride it was nearly colourless, heavier than water, and of a pleasant aromatic odour. Analysis showed that it was octylene dichloride.

0·2760 grm. chloride gave 0·4225 grms. silver chloride and 0·0100 grms. reduced silver

	Calculated	Found
Cl.	38·80	39·09

The portions of octane obtained after treatment with chlorine and with bromine were then mixed and repeatedly distilled over sodium. The mixed liquid commenced to boil at 118°, and about two fifths came over below 122°, the remainder distilling between 122° and 125°. Both fractions were immediately reddened by bromine vapour. The 122-125° fraction was analyzed with the following results:

0·2970 grm. hydrocarbon gave 0·9170 carbon dioxide and 0·4095 grm. water.

	Calculated	Found
C_8	84·22	84·20
H_{18}	15·78	15·32
	100·00	99·52

The specific gravity of this fraction was found to be [fol. 726] 0·7207 at 15° ·5; the fraction 118-122° had the specific gravity 0·7165 at 15° ·6. Zincke found 0·7124 at 16° for normal octane*.

*Ann. Chem. Pharm. vol. clxi. Ibid. p. 281.

Schorlemmer's dityrityl, which boils at 123-125°, has the specific gravity 0·7032 at 17°†.

Action of nitrogen tetroxide upon the octane and octylene boiling at 122-125°.—Many years ago Guthrie described a solid crystalline compounded of amylene and nitrogen tetroxide, $C_5 H_{10} (NO_2)_2$. So easily is this compound formed that the reaction of the gas upon amylene constitutes a very good test for the presence of the olefine, and comparatively small quantities of amylene may, by means of nitrogen tetroxide, be discovered and separated from considerable quantities of quintane.

We have studied the reaction of nitrogen tetroxide upon a mixture of octane and octylene in the hope of discovering an easier method of separating the two hydrocarbons. No solid nitro-compound, however, was obtained. On passing the gas into a mixture of the hydrocarbons it was rapidly absorbed and a heavy oil separated out; this had an odour resembling that of castor-oil; but the substance could only be preserved in the freezing mixture, and on distillation, even in steam, it was immediately decomposed.

8. The next well-defined fraction of the original liquid boiling between 100° and 200° distilled constantly at 145-148°. It was remarked that as this fraction increased in bulk, and the neighbouring ones became more free from octane and octylene, they gradually acquired a very characteristic and unpleasant smell, quite different from the fraction boiling at 122-125°. A portion of the mixed hydrocarbons was treated with bromine in the cold. The same darkening was observed as in the case of the 122-125° fraction; but it was by no means so marked as in that instance, and there was no difficulty in perceiving when a decided excess of bromine had been added. The following are the details of the experiment:

Hydrocarbon employed	18·95 grms.
Bromine needed	12·8 "
Equivalent to nonylene	10·0 "

As it was impossible to distill off the hydride, even in a current of steam, without at the same time decomposing the bromine compound, the liquid was treated with alco- [fol. 727] holic potash and distilled upwards for some time.

Water was then added, the dark brown oil separated, dried, and distilled; it commenced to boil at 150°, and fractions were collected between every 10°. The largest fractions came over at 160-170° and 200-218°.

The portion boiling between 200-218° on repeated distillation boiled almost entirely between 208° and 212°, and had approximately the composition $C_9 H_{17} Br$.

0·4165 grm. bromide gave 0·3370 grm. silver bromide and 0·0105 grm. reduced silver.

	Calculated	Found
Br.	39·0	36·3

The quantity obtained was too small to admit of purification.

A second portion of the liquid, boiling between 145° and 148°, was treated with fuming sulphuric acid. A considerable rise of temperature was observed, so that it was necessary to cool the mixture in order to prevent, as far as possible, the polymerizing action of the strong acid. The supernatant oil was then decanted, washed with dilute soda solution, dried, and distilled over sodium. About half the liquid came over below 170°, after which the thermometer rose very rapidly to above 340°, when the distillation was stopped. On cooling, the dense oily liquid in the retort solidified. The fraction boiling below 170° was redistilled over sodium; it boiled almost entirely between 145° and 150°. It was then mixed with the hydride obtained after treatment with bromine (see preceding section), and the mixed liquids were again distilled over sodium. The boiling-point was unchanged, the greater portion of the liquid distilling at 147-148°. This liquid is nonane, as the following analysis shows:

0·1970 grm. hydride gave 0·6080 grm. carbon dioxide and 0.2820 grm. water.

	Calculated	Found
C_9	84·37	84·16
H_{20}	15·63	15·92
	100·00	100·08

A determination of its vapour-density afforded the following data:

[fol. 728] Balloon with air	13·8050 grms.
Temperature of air	13·7° C.
Balloon with vapour	14·0525 grms.
Temperature on sealing	209°
Residual air	0
Capacity of balloon	116·8 cub. centims.

Vapour-density calculated for $C_9 H_{20}$ (H=1).	Found.
64·0	66·2

Its specific gravity was 0·7279 at 13°·5, compared with water at the same temperature.

It should be remarked that no liquid boiling at about 145-148° was discovered by Pelouze and Cahours in American petroleum. The nonyl hydride isolated by these chemists had the boiling-point 136-138°. We have assured ourselves that there is no liquid boiling at about this temperature in the products obtained from solid paraffin.

The boiling-point of the nonane isolated by us agrees perfectly with that calculated on the assumption that the differences in the boiling-points of the simpler members of the $C_n H_{2n+2}$ become continually less by 4°, until the well-known difference of 19° is obtained. (Schorlemmer.)

Calculated boiling-point of $C_9 H_{20}$ 146°. Found 147-148°.

Action of chlorine upon nonane.—About 15-20 grms. of the purified hydrocarbon were heated in a small flash fitted to an upright condenser, and a current of well-dried chlorine was sent through the liquid. The apparatus was placed in direct sunlight. The action appeared to commence immediately, the liquid darkened slightly in colour, and a large quantity of hydrochloric acid was evolved. The chlorine on passing into the heated liquid appeared to burn, a flash of light appearing at the end of the delivery-tube as each successive bubble of gas passed into the hydrocarbon. In order to prevent as far as possible the formation of high chlorinated products, the passage of the chlorine was occasionally interrupted and the liquid distilled; the portion boiling below 200° was set aside, and that which came over below this point was submitted to the

further action of the chlorine. Ultimately the greater portion of the liquid was found to boil between 200° and 230°, about 2/5 boiling above this point. By repeated distillation the former portion was divided into two portions—one boiling at 190-198°, and the other boiling constantly at [fol. 729] 240-245°. The first fraction on analysis gave numbers agreeing with the composition of nonyl chloride.

I. 0·6670 grm. chloride gave 0.5937 grm. silver chloride and 0.0100 grm. metallic silver.

II. 0·5195 grm. chloride gave 0·4930 grm. silver chloride and 0·0080 grm. metallic silver.

	Calculated	Found I	Found II.
Cl	21·9	22·5	22·8

The specific gravity of the nonyl chloride was found to be 0·8962 at 14°. Pelouze and Cahours found the so-called pelargyle chloride to boil at 196°; its specific gravity was 0·899 at 16°. It is highly probable, however, in spite of the concordance of these results, that the liquid obtained by us was a mixture of primary and secondary chlorides; and the same remarks is probably applicable to the product obtained by Pelouze and Cahours. The fraction boiling at about 245°. was in all probability $C_9 H_{18} Cl_2$, produced by the further action of the chlorine upon the hydride; the quantity, however, was insufficient to purify it for analysis.

9. The next well-defined fraction distilling at a constant temperature boiled at 170-172°. It was treated with bromine, with the following results:

Weight of liquid taken	4·80 grms.
" Bromine needed	3·38 "
Equivalent to decylene	2·95 "

The liquid was too strongly reddened by the bromine; it was evident that too great an excess had been added. This would make the amount of olefine too large. The quantity of hydrocarbon taken was too small; the experiment should have been repeated on a larger scale. Our object, however, was to economize our material, as we could find no ready method of separating the brominated compound from the

unattacked hydride without decomposition. Boiling with alcoholic potash gave a very indefinite result.

About 37 grms. of the mixed hydrocarbons were cautiously treated with nitric and sulphuric acids, and the mixture cooled to moderate the reaction. After standing about 17 hours the clear amber-coloured oil was separated, repeatedly washed, and distilled in a current of steam. When about ⅓ of the liquid had passed over, the remainder in the flash suddenly decomposed, becoming almost solid, and fumes of oxides of nitrogen were abundantly disengaged. [fol. 730] The distillate, which floated on water, was dried and distilled; it commenced to boil at 169°, and all came over below 175°, after repeated distillation over sodium, until the metal was no longer attacked; it boiled constantly at 166-168°.

It was analyzed as under:

0·2090 grm. hydride gave 0·6460 grm. carbon dioxide and 0·2950 grm. water.

	Calculated	Found
C_{10}	84·45	84·30
H_{22}	15·55	15·69
	100·00	99·99

Its specific gravity was 0·7394 at 13°·5, compared with water at the same temperature. Schorlemmer's amyl (decatyl hydride), obtained by the action of sodium on amyl iodide, boiled at 158-159°, and had the specific gravity 0·7275 at 14°. It is very probable that this hydrocarbon is not the normal hydride, but stands to the decatyl hydride boiling at 168° in the same relation that the amyl hydride boiling at 30° does to the isomer boiling at 39°, or as the ethyl amyl boiling at 90° (sp. gr. 0·6819 at 18°·5) does to the normal heptane boiling at 99° (sp. gr. 0·6915 at 18°). The normal decatyl hydride obtained by Pelouze and Cahours from petroleum had the specific gravity 0·735 at 15°; the hydride found by Greville Williams in the oil from boghead coal had the specific gravity 0.7365 at 18°.

A determination of the vapour-density of the decatyl hydride from paraffin gave the following data:

Balloon with air	13·9745 grms.
Temperature of air	12°
Balloon with vapour	14·2215 grms.
Temperature on sealing	222°
Residual air	0·2 cub. centims.
Capacity of balloon	105·5 cub. centims.

Vapour-Density Calculated for $C_{10}H_{22}$ (H = 1).

	Found
71	72·8

10. The next fraction of the liquid boiling below 200° distilled constantly between 192° and 197°, the greater portion of the liquid coming over at about 193-195°. The fraction boiling at 193-195° was treated with bromine, with the following results:

[fol. 731]

(1)	7·63 grms.	required 4·76 grms. bromine.
(2)	7·18 "	4·09 "
Mean	7·405 "	4·425

The fraction boiling at 195-197° was also treated.

7·04 grms. hydrocarbon required 3·85 grms. bromine.

Assuming that the fractions are mixtures of undecane and undecylene, 4·425 grms. of bromine would be equivalent to 3·78 grms. of the olefine, leaving 3·625 grms. of the hydride, or the fraction is a mixture of undecane and the undecylene in equal proportions.

A determination of the vapour-density of the 193-195° fraction gave the following data:

Balloon with air	13·2640 grms.
Temperature of air	16°
Balloon with vapour	13·5470 grms.
Temperature on sealing	261°
Residual air	0·8 cub. centims.
Capacity of balloon	113 cub. centims.

Found	81·1	Calculated	77·5

11. Fraction boiling between 200° and 300°.—By long-continued distillation over sodium the 2½ litres boiling originally between these limits were resolved into the following fractions:

(1)	212-215°*	
(2)	230-235°	solidifies at —14°·5†
(3)	252-255°	" 5°·5
(4)	273-276°	" +2°·0
(5)	290-295°	

The portion boiling at 300° (in the neighbourhood of 315°) is solid at ordinary temperatures.

The following details of the bromination experiments show that the fractions were invariably mixtures of olefines and hydrides:

Fraction 212-215°:

4·48 grms. required 2·65 grms. of bromine.

Fraction 230-235°:

4·23 grms. required 1·92 grm. of bromide.

[fol. 732] Fraction 252-225°:

(1) 9·38 grms. required 2·95 grms. of bromine.

(2) 8·605 grms. required 2·67 grms. of bromine.

(3) 5·13 grms. required 1·54 grm. of bromine.

Fraction 273-276°:

7·39 grms. hydrocarbon required 2·04 grms. of bromine.

12. It has already been mentioned that, on the first distillation of the oils obtained by splitting up the 3½ kilogs. of paraffin, a considerable amount of substance (which could not be distilled within the range of the thermometer) remained in the retort and solidified on cooling. This substance in its crude condition melted at 31°, but on recrystallization from ether the melting-point became higher. The whole of the substance was therefore cut up into small fragments, and spread upon filter-paper to remove adhering oil as far as possible, and repeatedly recrystallized from ether until the melting-point was unaltered.

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* These boiling-points are uncorrected.

†These points of solidification are only approximative.

It melted invariably at 41°·5 and solidified at 40°·5; it could not be distilled within the range of the mercurial thermometer.

It crystallized from either in beautifully white satiny scales, and gave the following numbers when burnt with oxide of copper in a stream of oxygen:

0·3035 grm. gave 0·9590 grm. carbon dioxide and 0·419 grm. water.

Carbon	85·19
Hydrogen	15·34
	100·53

Action of Bromine Upon the Solid Paraffin Melting at 41°·5.—A few grams of the substance were dissolved in bisulphide of carbon, and four minute drops of bromine added; this small quantity of bromine sufficed to colour the liquid strongly. On standing from 12 to 15 hours, the colour appeared unaltered, and the solution was not decolorized after heating from 60-70° for 12 hours. On heating the liquid to 150°, the colour disappeared after a few hours; and on opening the tube hydrobromic acid was evolved. About 10 drops of bromine were again added, and the liquid reheated to 150°; but no diminution in the red colour of the solution was perceptible, although on opening the tube dydrobromic acid fumes were abundantly disengaged. This observation would appear to indicate [fol. 733] that the hydrocarbon melting at 41°·5 is a member of the $C_n H_{2n+2}$ series.

Action of heat upon 41°·5 paraffin.—Repeated crystallization from ether having failed to alter the melting-point of this substance, and the behaviour with bromine evidently indicating that it belonged to the marsh-gas series, we considered that it would be interesting to study the combined action of heat and pressure upon it. The details of the experiment have been already given in section 1. After six distillations it was rendered completely liquid. It began to boil at about 40°, and about one sixth came over below 100°, about one third between 100° and 200°, and the greater portion of the remainder below 300°; the small quantity remaining in the retort solidified on cooling.

In a second experiment the action of bromine upon the liquid hydrocarbons was quantitatively determined:

Weight of liquid hydrocarbon taken	5·73 grms.
" bromine required before the liquid was reddened	30·7 "

The action of the bromine was very energetic, and it was necessary to moderate the reaction by cooling the liquid.

It is evident from these experiments that the solid paraffin (x C_n H_{2n+2}) had been split up by heat and pressure into a mixture of hydrides and olefines.

[fol. 734] TRANSLATION OF PETITIONER'S EXHIBIT No. 97

German Patent No. 37,728

Class 23: Pat Industry

A. Riebeck'sche Montanwerke, Actiengesellschaft, Halle a. Salle

Process for Separating off Light Hydrocarbons and Obtaining Viscous or Asphalt-like Oils from Paraffin Oils, etc., by Distillation under Relatively High Pressure

Patented in German Empire from February 28, 1886. Issued December 17, 1886

The process heretofore employed for the distillation of heavy dark paraffin oils (brown coal tar oils), crude petroleum or residues from the refinement of the latter, or of the tars obtained in the preparation of oil gas from paraffin oil or petroleum residues, are all subject to the objection that the yield in light oils, such as benzine and illuminating oils, is relatively small and that the high-boiling ingredients, left behind are in many cases of inferior value as lubricants and for other purposes. Thus, for instance, the heavy dark paraffin oils (brown coal tar oils) have heretofore been used only for the preparation of oil gas or the production of low-grade lubricants (axle grease). The possibility of making a rational use of the tars obtained in the prepara-

tion of oil gas from petroleum residues has heretofore also been precluded.

Numerous experiments on a large scale to subject such oils, residues, etc., to distillation under pressure, in the course of which extensive decompositions take place, have shown that by such a process the yield in excellent light oils (benzine and illuminating oils) is considerably increased and that the immediate residues obtained find a ready market as very good lubricating oils and asphalt oils.

The most advantageous pressure for the decomposition of the oils is quite definite for each kind, the yield in the different products and the losses due to gasification depending qualitatively and quantitatively on the degree of pressure. Experience has shown that for heavy paraffin oils (brown coal tar oils) the most suitable pressure is 3 [fol. 735] to 6 atmospheres according to the nature of such oils, for crude petroleum and its residues 2 to 4 atmospheres, and for oil gas tar 4 to 6 atmospheres.

The apparatus used for the distillation under pressure of the materials referred to consists of a distilling vessel fitted with a safety valve, inlet pipe, etc., a condensing coil and a valve. The distilling vessel is made of cast steel and has, generally speaking, the shape of the distilling vessels commonly used in the brown coal tar industry. When the parts swept by the fire are heated to a red glow, the vessel must continue to be impervious to the contents heated to about 400° at a pressure of 10 atmospheres. The tube of the condensing coil connected with the distilling vessel may be of less diameter than for distillation in a vacuum or under normal pressure.

The valve interposed between the distilling vessel and condensing coil is so arranged that it will open automatically and establish communication between the distilling vessels and condensing coil as soon as the pressure desired for decomposition is attained.

When fire is first started under the distilling vessel the connection between the distilling vessel and the condenser is left open by putting the valve in the proper position, until all the air has been displaced by oil vapors and the connecting pipe begins to heat. The valve is then adjusted for the required pressure and the distilling vessel more intensely heated. When the desired pressure has been at-

tained it lifts the valve, allowing the vapors to enter the condensing coils, in which they are condensed.

The effects of the above described distillation under pressure may be illustrated by the following results obtained in distillation on a large scale.

A dark heavy paraffin oil of 0.912 specific gravity at 17.5° c. and a viscosity (according to Engler) of 2.5 was distilled. 15% (by volume) passed up to 300°, the remainder at a higher temperature. The distillations under a pressure of about 3 atmospheres showed that the decomposition product distilling over does not vary essentially whether taken off from the contents of the distilling vessel in amounts of 30% or of .80%. It forms a brown very mobile fluid of 0.820 spec. grav. at 17.5° C. This decomposition product is absolutely equivalent to the crude illuminating oil of brown coal tar, and when treated with chemicals and distilled in the usual manner it yields a water white illuminat- [fol. 736] ing oil of 0.815 to 0.820 spec. grav., a f flashing point of about 30° c. and of great illuminating power.

When 25 to 30% of distillate is drawn off there remains a residue having a viscosity of 7 to 10, a spec. grav. of 0.930 to 0.950 and forming a profitable lubricating oil of good quality. When more than 30% is drawn off the residue becomes more and more asphalt-like, so that, when 50% of distillate is drawn off, there is left behind a black lustrous asphalt oil of 1.005 spec. grav. When 80% of decomposition distillate is drawn off the residue hardens into a coky asphalt.

For distillation under a pressure of 3 atmospheres the loss due to gasification, with 25 to 30% distillate drawn off, amounts to 4% (hence not much more than at normal pressure); with about 50% of distillate drawn off to 7%; and with about 80% of distillate drawn off to 15 to 18%.

When the process of distillation under pressure is applied to shale oil and petroleum, the best method is to abstract from the crude oils, by ordinary distillation, the light oils up to 70 or 75% residue and then to decompose the residue under pressure, drawing off about 50% of distillate. An Alsatian petroleum (Pechelbronn) of 0.880 spec. grav. treated in this manner yielded 15.32% more illuminating oils than with the usual distillation, being about one-half more than the usual yield. The residue is equivalent to that

obtained from the method of treatment heretofore employed and may be used in the preparation of asphalt or, when redistilled with super-heated steam, it can be made into lubricating oils.

When the distillation under pressure is applied to the tars left behind in the manufacture of oil gas, similar results are obtained. The yield in low-boiling oils amounts to about 2½ times the yield obtained with ordinary distillation, with a thickened residue, and without the formation of the usually obtained intermediate oils of 0.950 specific gravity.

Claim

Process for producing, by distillation under a pressure of at least 2 atmospheres, light hydrocarbons (benzine and illuminating oils) and simultaneously viscous lubricating oils or asphalt-like oils from heavy dark or light-colored paraffin oils (brown tar oils), crude shale oils and petroleum, residues from the refining of crude naphthas, from the tars resulting from the preparation of oil gas from paraffin oil or petroleum residues, and from all other mineral oils.

N.E.K.
5-3-15.
6-28-15 (8506).

[fol. 737] Translation of Petitioner's Exhibit No. 98

Berichte der Deutschen Chemischen Gesselschaft

Vol. 30, Pages 2919-2920

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This result is confirmed by the spec. gr. compared with the light refraction index of the different fractions before, and after, removal of the olefine, the benzins, and the naphthenes, and in this respect exhaustive determinations were made (see Gruening, Freiburg, Switzerland, dissertation).

Hence, apart from paraffins and ethylenes in the main, also naphthenes and benzin hydrocarbons are formed at comparatively low temperatures by the cracking process.

Dissociation Oils Resulting from High-pressure Distillation of Heavy Mineral Oils

(With the collaboration of C. Schneider)

The distillates which are obtained by the Krey process (G. P. No. 37728) as products of the dissociation of high molecular hydrocarbons deserve particular interest. Both from the petroleum oils with high boiling point as well as from heavy lignite oils, such as paraffin oil, etc., it is possible to produce light oils by high-pressure distillation, similarly as by the method of Thorpe and Young, and these light oils are useful as burning oils. The oil which Mr. Krey was kind enough to place at our disposal had been obtained from heavy lignite oils by pressure distillation, the pressure being as high as 6 atm. approximately, and the yield of this distillation process ranged between 30 and 60% of the raw material, according to how far the distillation was pushed.

This pressure distillate constitutes a rather mobile (fluid) liquid of a reddish-brown color exhibiting weak fluorescence, and giving off a disagreeable smell. Its spec. gr. was 0.8301. Elementary composition: C 84.67 and 84.83; H = 13.93 and 14.30; S = 0.80%. Boiling point:

Below 100°	100/120°	120/140°	140/160°	160/180°	180/200°	200/200°
4.0	4.5	5.0	6.7	7.6	9.0	9.5

220/240°	240/260°	260/280°	280/300°	Over 300°
11.5	12.6	12.8	8.6	8.0% by volume.

[fol. 738] Only the normal paraffins were isolated; but it is probable that also secondary and tertiary paraffins were present. From the different main fractions (whose boiling points were concentrated by the aid of dephlegamators) the olefines were combined with bromin, whereupon the non-bromated portions were distilled off; next the substances were treated with fuming sulfuric acid in order to eliminate the naphthenes as far as feasible, and they were finally fractionated repeatedly to obtain definite boiling points. In this way there were obtained:

Pentane: boiling point 37-39°, spec. gr. 0.6251 (20°). Found C 83.50, H 16.61. Calculated C 83.33, H 16.67. d=2.51 (calculated 2.49).

Hexane: boiling point 68-69°, spec. gr. 0.6670. Found C 83.55 H 16.12. Calculated C 83.72, H 16.28. d=2.94 (calculated 2.98).

Heptane: boiling point 97.5-98.5°, spec. gr. 0.69-24. Found C 83.91, H 15.85. Calculated C 84.00 H 16.00 d=3.44 (calculated 3.47).

Octane: boiling point 124-125°, spec. gr. 0.7124. Found C 84.20, H 15.58. Calculated C 84.21, H 15.79. d=3.90 (calculated 3.95).

Nonane: boiling point 148.5-149.5°, spec. gr. 0.7296. Found C 84.25, H 15.39. Calculated C 84.32, H 15.68. d=4.55 (calculated 4.43).

The proof of olefins was carried out with sulfuric acid and bromin substantially in the same manner as previously described. Ordinary concentrated sulfuric acid absorbs from the crude distillate from 34 to 35% by volume; hence, the same consists approximately 2/3 by volume of saturated, and 1/3 of non-saturated hydrocarbons.

In the several fractions there were found:

Fraction 35-40°: 8.25 grams consume 8.13 gr. bromine corresponding to 44% amylene.

Fraction 67-70°: 11.52 grams consume 9.61 gr. bromine corresponding to 41% hexylene.

to

Fraction 96-99°; 13.82 grams consume 9.80 gr. bromine corresponding to 43% heptylene.

The presence of naththenes may be taken to be extremely probab-e, judging from the change in spec. gr. and in the light refraction index of the different fractions of the oil prior to, and after, treatment with concentrated followed [fol. 739] by a treatment with fuming sulfuric acid. (For further details see C. Schneider, Giessen thesis.)

As regards benzol hydrocarbons, it was possible to demonstrate the presence of benzol in the form of nitrobenzol and by the fuchsin reaction in the fraction 75-90° and the presence of mesitylene and pseudocumene in the fraction 160/180° in the shape of the typical trinitromixture having a melting point ranging between 166-167°. By re-crystallization from benzol, the mixture could be separated into trinitromesitylene (fusion point 232°) and *and* trinitropseudocumene (fusion point 185°).

Also in the dissociation process by distillation of heavy lignite oils in the presence of high pressure, according to the findings obtained, the formation of paraffin-like hydrocarbons from hydrocarbons poorer in hydrogen must be assumed.

Karlsruhe Chemical Laboratory.

[fol. 740] TRANSLATION OF PETITIONER'S EXHIBIT NO. 99

Translation from Berichts Deutsche Chemische Gesellschaft, Vol. 21, pp. 1816-1827

331. C. Engler: Concerning the Formation of Petroleum

(Received May 28. Presented at the Meeting by W. Will)

Hans Hoefer (1) in his excellent work on "Petroleum and related substances came to the conclusion on geological grounds that petroleum must be of animal origin and that for its formation the remains of animals of earlier geological epochs, especially fish, saurians, coral animals, ink fish, mussels and other molluscs have contributed. It is well known that this hypothesis is not new as even ten years ago, the statement of Hoefer found its followers in Leopold v. buch, Bertels, Fraas, K. Muller and others and later in geologists who have been concerned with the ape*p*arance of bitumen or petroleum in America, as Wrigley Whitney, Hunts and others, moreover in Ch. Knar, Credner, Eck, Zinken, Paul, Tietze, Uhlig, Piedbeuf; and holding first place, the fatty substances developing in enormous masses [fol. 741] in the marine life of every animal are used as raw material for the formation of petroleum.

What especially interested me in the conclusions of Hoefer, who on account of his own rich experience is instructed as few others concerning the conditions under which petroleum is found in its numerous fields, was the proposition that from geological reasons—similar to those G. Kramer derived from the chemical point of view—petroleum could have resulted only with high pressure and not too high temperature, since this statement happened to be in agreement with the experiments that I intended to make relating to the decomposition of animal fats under great pressure.

I am giving here a short account of the results of my experiments up to the present, as they are perhaps capable of assisting in filling up a gap in the theory of the formation of petroleum from animal remains.

Dr. Krey, Director of the Riebeck Mining Co., of Webau, Saxony was kind enough to permit me to make my experiments with the aid of the apparatus patented by him (German patent 37728) which made possible the distillation at a pressure of up to 10 atm., for which I wish to offer him my thanks.

492 kilograms of brown North American train oil (from Menhaden, Clupea tyronn., caught on the west coast of North America, 1-1.5 kg. heavy) of sp. gr. 0.930 were subjected to distillation in the apparatus. With an original pressure of about 10 atm., which however, descended to about 4 atm. in the course of the operation, and an original temperature of 320°, towards the end somewhat above 400° C., besides combustible gases a distillate passed over which separated into a lower hydrous and an upper oily layer. The latter was collected in fractions and those which with testing showed a still considerable portion of unsaturated fats or fatty acids (in all 217 kg. of the distillate) were subjected to another pressure distillation. In all 299 kg. of oily distillate was obtained which corresponded to an output of about 60%. About 20 kg. hydrous distillate was collected but unfortunately it was impossible to prevent considerable amounts of steam and light boiling oils to be carried along by the gas current which was at times very powerful. Still the condensation was so efficient that the oil after surface purification began to boil even at 34°.

[fol. 742] The crude oil distillate is of a brownish color, transparent in thin layers, with very green fluorescence and without unpleasant odor; the pungent odor of acrolein is lacking. Sp. gr. 0.8105. Upon agitating, it gives:

To water	0.4% Vol.
" potassium lye	4.8%
" Engl. sulfuric acid	20.8%
" Mixture of Engl. & fuming sulfuric acid	9.6%

A fractionated distillation of 100 ccm.—81 gr. of the crude oil according to the method described by me elsewhere gave in distillates:

	To 125°	125-150	150-175	175-200	200-225	225-250	250-275
ccm	21.5	8	10	6	9.5	10.5	11
gr	15.5	5.5	7.5	5	8	9	9

	275-200	Over 300	
ccm	10.5	13	(residue plus loss).
gr	8.5	13	

thus in main fractions:

	Under 150°	150-300	Over 300
Volume-perc	29.5	57.5	13
Weight	25.9	58.0	16.1
Sp. gr.....	0.712	0.817	....

First, the part boiling under 150° was subjected to a more thorough examination. For purifying, I treated it successively, and occasionally with repetition, with concentrated sulfuric acid, then a mixture of 2 parts English and 1 part fuming sulfuric acid and finally with sodium lye and water. 37% volume disappeared by agitating with sulfuric acid which as the fatty acids boiling under 150° must be found mainly in the hydrous distillate, gives an approximate basis for the mixture proportions of the hydrocarbons (saturated and unsaturated) contained in this oil fraction. During the examination of the latter (as well as other parts of the work) I first of all separated the former, present in different main amounts, by fractional distillation, as possible, and in this way isolated the following hydrocarbons.

Normal pentane with boiling point 36-38°, sp. gr. 0.622, vapor density 2.51, carbon 82.81, hydrocarbon 17.10, (calculated 83.3 or 16.7) % which values correspond satisfactorily to those given heretofore for pentane. Neither bromine nor hot fuming nitric acid act on the hydrocarbon so that its identity is established indubitably.

[fol. 743] Normal hexane, boiling point 68-70°, sp. gr. 0.664, vapor density 2.876, carbon 83.40, hydrogen 16.58% (calculated 83.72 or 16.28%). On this hydrocarbon as well as on the following, there is no action of bromine and slightly heated nitric acid.

Normal heptane, boiling point 97-99°, sp. gr. 0.688, vapor density 3.35, carbon 83.79%, hydrogen 16.29% (Calculated 84.0 or 16.0%).

The hydrocarbons octane and nonane of the normal series are likewise already known according to their boil-

ing point and sp. gr. but have not been examined in detail. Moreover, the behavior during the distillation leaves me no doubt that hydrocarbons of the secondary series are represented, in short we have here to deal with the material which is called the "inextricable mixture" of hydrocarbons of petroleum by Schorlemer.

As train oil is a mixture of triglycerides, mainly oleic acid and moreover palmitic acid, stearic acid and fatty acids poor in carbon, it must be of interest to learn the behavior of the different glycerides in pure state under like conditions. Therefore, I have first subjected tri-olein and tri-stearine to a pressure distillation in small amounts. The glycerides were made artificially and purified as pure oleic acid or stearic acid with pure glycerin according to the Berthelot method. As apparatus I used glass tubes bent at an obtuse angle, each charged with about 30 gr. of the substance, then fused shut and inserted in a digester so that the empty leg, bent downwards, projected outside. After heating for about four hours at about 350 deg., the tubes were removed, the gases let out and this operation repeated (on an average 4 times) until upon formation of a sufficiently light-flowing product the reaction appeared ended. Preliminary tests with train oil had shown that the reaction is exactly similar to that with the pressure distillation in the Krey apparatus.

Tri-olein gives besides water a light oily product which develops gas even at ordinary temperatures, begins to boil perceptibly at about 300° and contains about 50% in weight of parts boiling under 300°. The residue from the distillation upon repeated treatment in the closed tubes then gives more volatile oils so that by repeated treatment, the tri-olein can be changed almost completely into products of dry distillation. It should be mentioned here that in certain tubes only a very small amount of residue re- [fol. 744] mained after repeated heating of the olein under pressure, the olein thus under certain conditions changing nearly entirely into volatile distillate and gases without removal of parts of the distillation products.

Tri-stearine, treated in the same way, gives about 60% of oils boiling under 300°. Otherwise, the behavior is the same as with the olein, only great quantities of stearic acid distill at the beginning in the cold portion of the tubes.

Although it can be assumed from general reasons that the fatty acids participate alone in the formation of volatile hydrocarbons, it still appears important to verify by some direct experiments of heating free fatty acids alone the analogy of the course of the process. Pertinent observations are to some extent available without however offering a satisfactory answer to the question, as is evident from the contradictory statements in our textbooks and handbooks. Gottlieb (2) in 1846 called attention to the hydrocarbon occurring with other products in the distillation of oleic acid, likewise W. Heintz (3) in 1855 observed the formation of small amounts of hydrocarbons of the ethylene series in the distillation of stearic acid in a hydrogen current and Fremy and especially Berthelot (4) noticed the occurrence of ethylene hydrocarbons among other products in heating oleic acid alone or with alkaline bases. Bolley and Bergmann (5) obtained a like result upon heating oleic acid to 320°. Cahours and Demarcay (6) moreover isolated liquid fatty acids with low carbon content (baldrianic acid, capronic acid, etc.) and saturated hydrocarbons (pentane to nonane) from a by-product which was obtained in the Fournier stearine factory from crude fatty acid distilled in superheated steam and product of sulphuric acid saponification; and finally G. Johnston (7) succeeded in disassociating stearic acid by distillation of solid paraffine under pressure in a way similar to that of Thorpe and Young (8), i. e. by superheating in a tube placed on one side in a gas combustion furnace and effecting the cracking into water, carbonic acid, paraffine, olefine and ketone.

If the free fetty acids are heated in the above described way to 350° or a little more, with oleic acid there is obtained very soon, besides water, light hydrocarbon oils just as with olein and train oil and when stearic acid is heated exactly the same result is given. The last result proves the observation of Johnston in contrast with that of Berthelot, the latter stating that under these conditions, stearic acid does not undergo any decomposition. If stearic [fol. 745] acid is heated in closed tubes for several hours at 350° so that the whole tube rests in the digestor, there is no possibility of condensation of the volatile decomposition products in a cooler part of the tube and, as I ascertained

by experiment, no change in the stearic acid can be noticed, especially no development of gases, while the formation of liquid decomposition products begins at once when a part of the tube, bending downwards, projects outside so that the products of disassociation can condense. With oleic acid on the contrary, and likewise with train oil, the decomposition takes place even in a pipe heated throughout. Gases and even combustible gases, chiefly swamp gas with which however there is always mixed a little carbonic acid, likewise water are to be noticed if above all decomposition or formation of hydrocarbons has taken place.

A distillation of the train oil used for the above experiments in a vacuum shows how different its behavior is upon heating at low temperature. Train oil distills over to 4/5 of its weight with generation of combustible gases and the distillate stiffens to a light-yellow butter-like mass which contains only about 10% hydrocarbon, and moreover is completely saponifiable: water appears in only exceedingly small amount.

By the observed behaviour of animal fat in heating under pressure to not too high temperature and especially by the surprising result of obtaining 60% of weight of the fat in crude oil, which to more than 9/10th consists of hydrocarbons, there appears to me that a new witness to the truth of the theory concerning the formation of petroleum from animal remains has been found.

If it is considered that there are weighty arguments against the formation of petroleum by inorganic means as Berthelot, Bryasson, Mendeljew and others have contended, (9), there remains only the assumption that dead plants or animals have contributed the raw material for the formation of petroleum. If the formation from plant remains is assumed, there must have been a process of dry distillation, even though at low temperatures—as G. Kramer correctly deduces from the chemical properties of petroleum. Then however, there would be coal-like plant residue in the neighborhood or in some recognizable relation to the petroleum fields—assuming secondary fields, which has not been the case with all the important oil fields examined up to the present. On the other hand it would be expected that in [fol. 746] coal beds or the neighborhood of the same, liquid hydrocarbons or other bitumens should appear oftener and

in larger quantities. However this assumption is not met either as where liquid hydrocarbons are inclosed in coal beds or trickle out of the same, it is found upon further consideration that they never appear in the bed itself but that the oil occurs rather in other layers, as for instance at the well-known coal beds in Wombridge, England, in sandstone or inside coal beds in combination with strata which show animal remains and it is lacking in the coal districts, above all in all mineral coal districts.

On the contrary it has been determined that wherever petroleum is found in primary fields, plant remains are not seen at all or only in very unimportant amounts but on the contrary animal remains or undoubted traces of the same are regularly seen. Of special interest from the chemical point of view are the ortho ceratites in the Trenton limestone at Packenham in Canada, whose living chambers sometimes contain up to several ounces of petroleum, as demonstrated by T. St. Hunt, and likewise the occurrence of petroleum observed by Fraas as a kind of exudation of coral reef now projecting above the level of the sea, on the shore of the Red Sea near Djebel Zeit. Similar observations have been made with fossil corals in Canada with Carpathian fish schists and even in mussel limestone, small cells filled with petroleum have been again found. Finally Hoefer calls attention to the fact that all schists which produce large amounts of hydrocarbon oil upon dry distillation are rich in animal remains while they show relatively small amounts of plant remains, and that minerals containing large amounts of plant remains are as a rule not bituminous but they usually become bitminous as they include animal remains.

That petroleum originates from marine fauna (assuming animal origin), is corroborated not only by the animal remains in geognostical relation to the same, but also by a whole series of other circumstances, among which the water containing common salt usually gushing out or pumped out with the petroleum does not play a minor part.

It is perhaps not untimely to describe more in detail the formation process of petroleum from animal remains from a purely chemical standpoint. As chemists *and* more accustomed to working with plant substances, we are inclined to consider them as the foundation of the formation of

petroleum likewise. If however the paleontologists *but* [fol. 747] immeasurable amounts of animal substances at our disposal, as is easily done considering the great mass of their fossils, the question of the formation of petroleum from animal remains—disregarding geognotic relations—warrants the same claims as that of formation from plant remains.

I proceed from the assumption that the question put by G. Främer (10) as to whether different temperature and pressure conditions govern in the formation of the paraffine and naphthene contained in petroleum, should be answered in the affirmative according to his own example, that furthermore both from the character of the substances composing the petroleum and from the lack of carbon-like residue a distillation process at considerably lower temperature must be assumed and perhaps more probably, that the pressure at which the hydrocarbons of petroleum were formed from animal remains was often such that it often caused the condensation of the products formed. In this relation, I recall my experiment in which I succeeded in disassociating train oil for the greater part into hydrocarbon oils, water and by-products by heating to 350° in closed tubes without an extension serving for condensation of the oils formed. Just as in these closed tubes, it is possible that the animal substance of earlier geological epochs has been subjected to this high pressure surrounded by impermeable layers and in closed receptacles. In view of the sedimentary starta deposited above the petroleum fields, we do not lack proof positive of such a pressure, as Hoefer has already said. The artho ceratite chambers at Packenham filled with petroleum are such receptacles on a small scale. It is not impossible that in certain cases the pressure of the sea water above the starta has cooperated, the coral banks of Djebel Zeit with their exudations of petroleum observed by Fraas appear to me to be proof of the fact.

The lack of a series of chemical compounds which, as for instance acrolein, allyl compounds, fatty acids with less carbon content than products of fat decomposition, it would seem should be present, is not astonishing if it is taken into account that with thousands of years contact of the petroleum with water, those substances soluble in water

would long ago have been washed out, without considering that glycerine, as given more in detail below, can have been separated out and carried off even before the formation of petroleum. Testing of crude petroleum in this relation [fol. 748] from indubitably primary fields would be of greatest interest.

On the contrary it seems astonishing at first thought that nitrogen is lacking in petroleum. However, this discrepancy even though not in the same degree would still appear extraordinary if petroleum originated from plant remains, although the latter contain considerably less nitrogen, since we know that in the products of their dry distillation not inconsiderable amounts of nitrogen compounds are present. Disregarding the bases contained in the true animal, all the nitrogen of our ammonia and its salts originate from coal, thus form such plant remains. Nitrogen, however, cannot be noted as entirely lacking in all petroleums, it has rather been positively detected in a series of such oils, i. e. by Peckham in several American oils, by St. Claire-Deville and Boussingault in Alsacian crude oil, by the latter investigator in a petroleum from China (Ho Tsing) likewise, by Delease in mineral tar from Trinidad etc., Feodorowicz noticed ammonia in petroleum from Siary (Galicia) and Carnegie observed crystals of ammonium carbonate in the gas wells of Pittsburg.

In this connection however, one point should be referred to which appears to me to have received too little consideration in all former examinations of this question, which however upon closer inspection appears natural,—that the occurrence of nitrogen in crude petroleum is the exception. While I am very well acquainted with the fact that in the chemical nature of the chemical compounds composing animal substance and plant substance there is no very sharp difference, that plants, for instance, carry substances containing nitrogen, fats etc., as important constituents for their life and propagation as well as the animals it is however clear that in the organic substance of the animal world there is more question of the presence of two contrasting substances as it were than with plants; while the latter show a certain unity in their main mass, the former consist of concurring parts of nitrogeneous muscle substance and fat free from nitrogen, in their main mass, especially

the sea animals which are chiefly under consideration here. The durability of these two substances is however very different; the nitrogenous substances rapidly succumb to rot and decomposition, the fats do not. It is certainly to be assumed not unqualifiedly that in the agglomerated animal corpses of prehistoric world the decomposition went on in two main phases: that first the nitrogenous substances de- [fol. 749] composed, the nitrogen being volatilized as such or in the form of ammonia and its compounds or perhaps in still more complicated forms or being carried away by water, that the fat remained behind (it being not impossible that in certain cases the fat was carried to secondary beds) and only at a later time was converted to petroleum by pressure and heat, perhaps chiefly by the former. In this relation I recall the research of Gregory (11) but more especially Wetherill's (12). The latter found in the fossil bones of the American bison 86.3% fatty acids and some coloring matter, 10.1% lime with a trace of phosphate salts and 3.6% "flaky organic substance" and in a great number of cases of burying corpses, all of fat men, in wet ground noticed that the decaying process left behind a wax-like substance "adipocere" or fat wax, consisting chiefly (97-98%) of fatty acids. He obtained a similar result with a sheep buried for 10 years. In no case however, did he find ammonia in the remaining material. Even before him, Gregory found, in the remains of a pig buried 15 years before, an adipocere as residue which was one-fourth stearic acid and three-fourths palmatin acid ("margarin acid") and oleic acid, even the bones had in this case already disappeared. Finally, direct experiments by Wetherill yielded that when animal substance (an ox heart) artifically undergoes rotting or decay, the nitrogenous substance disappears and only the fat remains behind in the condition of adipocere. These cases are sufficient to prove the durability of animal fat whether the glycerine is already separated off or not.

If we now imagine sedimentary mineral intermingled with fatty material of this kind, the remains of decayed animal bodies, and subsequently subjected to great pressure, or placed in heat, an explanation of the formation of petroleum is given. It is possible that the ammonia of the petroleum of Siary and the ammonium carbonate of the

natural gas wells of Pittsburg are remains of the nitrogenous substance of prehistoric animals obtained as an exception; the presence of nitrogen in petroleum is not a necessary result of the formation from animal remains.

The lack of coal-like residue in the petroleum itself or in genetic relation thereto, could not be made to harmonize with the theory of the formation of petroleum from organic substances. This condition however is a great deal more unfavorable to the formation from vegetable substances than from animal substances. If cellulose ($C_6H_{10}O_5$) is [fol. 750] taken as representative of the former, we have in it 44.4% carbon, 6.2% hydrogen and 49.4% oxygen. If even only a small part of these elementary substances are allowed to come together as water, there remains a residue which is so poor in hydrogen and so rich in carbon that without separation of carbon a formation of saturated hydrocarbons or even the series C_nH_{2n} can no longer be thought of. For general reasons however it is probable that the higher the pressure and the lower the temperature in comparison, the more water and the less carbonate acid is formed during disassociation. The more water that is expelled from the wood substance however, the more carbon must necessarily remain behind. That hydrocarbons can nevertheless be formed from cellulose, remains of course undisputed, I only maintain that their formation is impossible without coal-like or carbonaceous remains being left as residue.

It is entirely different with the animal fats or the fatty acids resulting therefrom by glycerine separation. The following are obtained:

	Tri Stearine	Tri Palmitine	Tri Olein	Stearic Acid	Palmitic Acid	Oleic Acid
C	76.6	75.9	77.4	76.1	75.0	76.6%
H	12.4	12.2	11.8	12.7	12.5	12.1
O	11.0	11.9	10.8	11.2	12.5	11.3

Train oil likewise keeps approximately within the above limits in its elementary composition. If all the oxygen and the hydrogen necessary for water is eliminated from these fats or better fatty acids, carbon and hydrogen remain behind constantly in a ratio (about 87% carbon and 13% hydrogen) which is not only not far from the whole composi-

tion of our crude petroleum but rather is astonishingly close. I refer in this connection to the analyses of Markownikoff and Ogloblin (13) who found in petroleum from Baku:

	I	II	III
C	86.65	87.01	86.89%
H	13.35	13.22	13.18%

and furthermore to the numerous analyses of St. Claire Deville (14) who found in the petroleum from:

[fol. 751]

	C	H	O
Pechelbronn (Alsace)	85.7	12.0	2.3%
Schwabweiler (Alsace)	86.2	13.3	0.5
Oedesse (Hannover)	80.4	12.8	6.9
Wietze (Hannover)	86.2	11.4	2.4
East Galicia	86.2	12.1	5.7
West Galicia	85.3	12.6	2.1
West Canada	84.2	13.4	2.3
West Canada	84.3	13.5	2.0
West Virginia	83.2	13.2	3.6
West Virginia	83.6	12.9	3.5
Walachia	83.0	12.2	4.8
Piedmont	86.4	12.2	1.4
Zante	82.6	11.8	5.6
Burmah	83.8	12.7	3.5

If in these result of analyses, account is taken of the oxygen with the hydrogen necessary for forming water with it and the remaining carbon and hydrogen is reckoned by percentage, numbers which are not far from 87% carbon and 13% hydrogen are always obtained.

From these considerations it is likewise explained why we never find coal-like residue in conenction with the petroleum fields. The decomposition of the fats or fatty acids takes place with very high pressure without the formation of such residue, attention being called to the above-mentioned surprising observation that the conversion of fats in closed tubes under pressure often occurred without any considerable formation of carbonaceous residue.

Finally I cannot concur in the conception that petroleum originates from plant remains even on general grounds, as is is known that plants play only a very subordinate role in marine life; they are met with on the shores, but the conditions for their existence disappear even at depths of 30-40 m. and therefore only in the neighborhood of the coasts can great accumulations of plant remains be formed—disregarding those submerged. The Sargassum-algas which float about on the sea as floating islands occur so sporatically that their appearance must be considered as a disappearing minority in contrast to the marine world.

Karlsruhe, May. Chemical laboratory.

[fol. 752] (1) Hoefer in Bolley's Technology "The Mineral Oil Industry" H. Houfer and F. Fischer, I edition p. 101.

(2) Ann. Chem. Pharm, 57, 33.

(3) Poggend. Annal. 94, 272

(4) See Compt. rend., 89, 336.

(5) Ding. Polyt. Journ. 179, 463.

(6) Compt. rend. 80, 1568; 89, 331.

(7) This Berichte VIII, 1465.

(8) " " V, 556.

(9) see Hoefer, p. 101.

(10) This Berichte XXI, 608.

(11) Ann. Chem. Pharm. 61, 362.

(12) Jahresber. f. Chem. 1855, 517. Journ. f. pr. Chem. 68, 26 following. Transact. of the American Philosoph. Soc. XI.

(13) This Berichte XVI, 1874.

(14) Compt. rend. 66, 442; 68, 485; 69, 1007. See likewise Jahresberichte für Chemie 1869, 1126.

Tr. MMJ.
6/17/25.

[fol. 753] TRANSLATION OF PETITIONER'S EXHIBIT No. 100

Berichte der Deutschen Chemischen Gesellschaft

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Formation of Olefine, Naphthenes, and Benzol Hydrocarbons by the Distillation of Fats under High Pressure

By C. Engler and Th. Ishmann

(Received October 13)

In earlier publications (see this paper, Vol. 21, p. 1816 and Vol. 22, p. 592), one of the Authors has demonstrated that in the pressure distillates of fatty substances there are found a great number of light and heavy hydrocarbons of the paraffin series, among them also solid paraffin and lubricating oils, and from the further behavior of those distillates the inference could be drawn further that also olefile, and apparently also nap thenes, are contained therein. Now, this assumption has been confined by the following investigation; also the presence of benzol hydrocarbons could be proved. (For further details see inaugural dissertion of Theod. Lehmann, Freiburg, Switzerland, 1897.)

The proof of the olefins was effected in the main according to the method previously used by Thorpe and Young as later elaborated by Hensler. The approximtae total quantity of olefins had previously been ascertained in the local laboratory by absorption with concentrated sulfuric acid, the quantity in the lighter portions having been determined to be 37%. Now, since against this method—and quite justifiedly so—the objection could be made that polymeriza-

[fol. 754] tion might take place on account of the sulfuric acid, a fact, that if true, would vitiate the accuracy of the results, we repeated the tests on the portions of fish-oil pressure distillates boiling below 75°, those boiling between 75 and 100°, between 100 and 125°, between 125 and 150°, and between 150 and 175° by the application of the bromation method.

The different fraction were diluted with a little anhydrous ether or carbon disulfid, then strongly chilled, and

then additions of bromine dissolved in ether or carbon disulfid from a burette made as long as the color was noticed to disappear rapidly. Whatever excess of free bromin was left over could easily be removed by means of a current of air, whereupon the whole mass was distilled with steam. After the light portions floating on water had been driven off, the heavy bromides were collected separately, the steam distillation being thereupon repeated twice in order to separate off as rapidly as possible whatever non-bromated hydrocarbons had been left over. The quantities of bromin used for combining with the olefins were:

For fraction	45–75°	75–100°	100–125°	125–150°	150–175°
Quantity used	118	208	300	221	101
Bromine consumed...	64.8	120.6	157.6	107	45.6
Corresponding in % to	29	30	32	35.5	34
Or	hexylene	hexylene 35 heptylene	heptylene 37 octylene	nonylene 38 nonylene	octylene 39 decylene

Whence it can be seen that the method of determining the olefins by the aid of bromine gave about the same results as with the use of sulphuric acid (upon the average 37%). It is furthermore shown that, in agreement with the results obtained by the dissociation of heavy oils, the quantity of the olefins grows relatively as the boiling point of the oils increases.

The crude bromide separated in a manner as hereinbefore described were dried and rectified in the vacuum apparatus at from 10-12 mm.; but even by repeated rectification only fractions of wide range could be obtained.

The spec. gr. and composition of these fractions are summarily shown in the following Table.

[fol. 755]

	42–50°	50–60°	60–70°	70–80°	80–88°
Spec. Gr. (15)	1.6427	1.5821	1.5563	1.5249	1.5114
Br.	67.66	65.22	63.96	62.71	61.64
G	.....	30.07	.....	32.23	.....
H	.....	5.02	.....	5.41	.....

	95–105°	112–125°	125–132°
Spec. gr (150)	1.4685	1.4263	1.4120
Br	59.36	57.07	56.20
C	34.34	.....	.....
H	5.57	.....	.....

Fraction 125/132° showed already marked dissociation of hydrobromic acid.

Calculated composition of dibromids of:

	Amylene	Hexylene	Heptylene	Octylene	Nonylene
Br	69.5	65.57	62.00	58.83	55.94
C	....	29.51	32.55	35.29	37.26
H	....	4.92	5.45	5.88	6.29

It will be noted that fraction 50/60° corresponds quite exactly to the hexylene bromid, and fraction 70/80° to heptylene bromide. The other fractions seem to be mixtures of higher and lower homologous olefin bromide.

The proof for naphthenes by determining the refractive index of light customarily applied to other oils failed to furnish reliable results in this case; hence, we were compelled to ascertain the presence of naphthenes according to the method suggested by Kraemer and Housler, namely, from the composition of fractions of definite boiling points, from which by prior cold treatment with bromine and by distiling off the more volatile non-attackable hydrocarbons with aqueous vapor, the oelfins, then with sulfuric acid and nitrosulfuric acid and the balance of nitro-products resulting therefrom with tin and muriatic acid, then the aromatic hydrocarbons, were removed. The oils after washing with solda solution and drying with calcium chlorid were then fractionated, and were then determined as follows:

Fraction	68.5–69.5°	70–80	98–99°	123–124°
Spec. Gr (15°)	0.6752	0.6805	0.6985	0.7170
C	83.98	84.15	84.44	84.56 %
H	16.23	16.10	15.65	15.58

Fraction	149.5–150.5°	160–162°
Spec. Gr. (15°)	0.7215	0.7328
C	84.66	84.67%
H	15.43	15.48%

The naphthenes showed together C = 85.71, H = 14.29%, while the paraffins had this composition:

[fol. 756]	Hexane (69°)	Heptane (98°)	Octane (125°)	Nonane (150°)
C	83.72	84.21	84.37	84.40
H	16.28	15.79	15.63	15.50

	Dakane (175°)
C	84.51
H	15.49

In the first place, increasing carbon and decreasing hydrogen with growing boiling point and the elementary composition coming close to the paraffins with correspond-

ing boiling points, go to show that the above fractions, as found previously consist substantially of paraffin hydrocarbons; still, since the carbon content is throughout somewhat higher, and the hydrogen content lower (while in the ordinary run of the analyses the opposite would be true), this tends to indicate the presence of naphthenes. In order to isolate these in pure condition, considerably greater quantities of distillates obtained by the high-pressure process from fatty substances would be required than had been at our disposal because of the difficulties attendant upon their production.

But the presence of benzol hydrocarbons could be safely demonstrated in the pressure distillation of fish-oil; benzol in the fraction 76/83° by nitration (the smell of nitrobenzol being clearly noticeable), then reduction into anilin and the use of the chlorid of lime test and by the conversion of aniline to benzylidenanilid (melting point determined at 44°) and into acetanilid (fusion point 113°); toluene in the fraction 106/114° by nitration as 2-4 dinitrotoluene (melting point 70°); m-xylene as trinitrometaxylene (fusion pt. 178°) in fraction 130/138°, while the presence of mesitylene and pseudocumene seems to be indicated only by the formation—though this is a characteristic and significant fact—of a mixture product of the two trinitro-derivatives (fusion point 170°) by the nitration of the fraction 160/-169°.

Together with the results previously published, it can be said that in the products of pressure-distillation of fish-oil the presence of hydrocarbons of the paraffin series (liquid and solid), of the ethylene series, and the benzol series has been proved reliably, while the presence of naphthenes may be taken to be highly probable; and since in our experiments pure glycerids and other fats and oils generally showed the same behavior as fish-oil, the reaction may be considered to hold generally for all fatty substances. The formation of cyclic hydrocarbons, especially of the benzol series, from fatty substances at such comparatively low temperatures may not be without general interest.

Karlsruhe, Chemical Laboratory.

[fol. 757] TRANSLATION OF PETITIONER'S EXHIBIT No. 101

Berichte der Deutschen Chemischen Gesselschaft

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Detection of Paraffin and Lubricating Oil in the Pressure Distillates of Fish-Oils

By C. Engler and L. Singer

(Communication from the Chemical Laboratory of Karlsruhe Technical University)

(Received on June 5; read before the meeting by H. Jahn.)

The point has been raised in various quarters in connection with the theory of petroleum formation from remnants of animal fats, that in the pressure distillates of natural [fol. 758] glyceride and higher fatty acids investigated in the local laboratory neither paraffin nor lubricating oils have been found. As a matter of fact, in a test made at the very beginning we were unable to discover paraffin in the pressure distillates of fish-oil. To the determination by analysis of lubricating oil in the higher fractions we did not ascribe any great importance, we therefore did not use much care in its isolation. Now, the emphasis that has again in more recent times been laid upon these gaps induced us to resume our investigations along these particular lines, especially since an ample amount was still available of the fish-oil distillate which we had obtained by the kind cooperation of Dr. Krey, of Webau.

Much to our surprise a crystalline separation was noticed in the different portions of high-boiling-point residues of fish-oil pressure-distillates kept in some small and larger containers which had never been observed before, and which evidently was produced only then because previous to that time the weather had been extremely cold, the distillated having been subjected to this cold for some prolonged period of time in unheated store rooms. It was easy to demonstrate that these crystalline separations, as a matter of fact, consisted of paraffin, and not possibly of non-dissociated solid glyceride or fatty acids.

This led us to resume the direct analysis of our crude pressure distillates; however, while the Zaloziecki method is usually very reliable (see Dingler's polytechnisches Journal, 267, p. 274), we failed to obtain from the distillates other than amorphous masses flowing even at ordinary temperature. Also the examination of the fraction boiling over 300° gave no better results.

However, when the portions of high boiling point of the fish-oil distillate, after removal of all traces of non-dissociated fatty substances by the aid of soda lye, had been exposed for weeks in succession to the cold of the winter or to artificial chilling, on remelting the solidified masses, it was readily possible to find solid crystalline paraffin, which drawn off by suction at low temperature, by repeated dissolution in ligroin re-precipitation with 75% alcohol, and treatment in ligroin solution with animal charcoal, was obtained in the shale of white crystalline masses having a melting point ranging between 49 and 51°. Analysis showed the following results (specimen I directly, and specimen II after renewed purification by conducting carbonic acid through the refused paraffin):

[fol. 759]

	I	II
C	85.70	87.70
H	13.54	13.10

In view of these findings, the proof that paraffin is formed in the distillation of fatty substances in the presence of high pressures may be taken to have been furnished.

Now, in order to demonstrate also the presence of lubricating oils, a few kilos of the crude pressure distillate were shaken with soda lye, next with water and sulphuric acid, and finally with water, then distilled, the different fractions being again washed with solda lye (concentrated), water, sulfuric acid, then water, solda lye, and water, and again subjected to distillation; the heavy oils were then transparent, light-brown in color, while they exhibited marked fluorescence after washing with soda lye. The heavy oils during their chemical purification should be advantageously diluted with ligroin as otherwise the action of the sulfuric acid would be unduly strong.

In comparing the viscosity of the ensuing oils with water, because of the small quantities involved, a small glass vis-

cosimeter with an extrusion hole of 1 mm. width was used, from which the water was found to run out, at 20°, 13 seconds. Taking this time as unity, the oil fraction passing over between 290 and 300°, when heated from *from* 50-60°, exhibited a specific viscosity of 1.6 while for single fraction above 300° C, the viscosity was as high as 3.4, at the same temperature, which goes to show that the presence of lubricating oil is proved beyond doubt.

An unfortunate point is that the constitution of these oils possessing high boiling points is not determinable, and it cannot be said, for the time being, whether they agree with the lubricating oils obtained by synthetic means by Kraemer and Spilker (see this paper, 24 p. 2785), and whether their formation is associated possibly with the glyceride or allyl compounds formed therefrom.

As regards the identity in properties of the pressure distillates of fish-oil with natural petroleum, we believe we must call attention to tumernol-sulfon and tumenol-sulfonic acids proved to exist separated recently by E. Dieckhoof (see Dingler's Polyt. Journal, 274, p. 41) in the products obtained by the action of funing sulfuric acid upon pressure-distillates of fish-oil, which, in their properties and in their composition, perfectly agree with the tuminol bodies separated by A. Spiegel from natural petroleums.

[fol. 760] TRANSLATION OF PETITIONER'S EXHIBIT No. 102

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The Dissociation of Viscous Substances Lubricating Oils by Pressure Distillation

By G. Kramer and A. Spilker

(Received July 11)

In the study published by us last year regarding the nature of petroleum, the possibility has been discussed by us to demonstrate by the pressure-distillation process and

the study of the ensuing dissociation products, the nature of lubricating oils and paraffin oils of high boiling point. Now, tests in that direction have been made by the Authors, and we have come to the conviction that this method is practicable for certain substances related to the said oils. However, we did not succeed in throwing light on the constitution of the said mineral-oil hydrocarbons in this manner, and in realizing what we are really aiming at; indeed, we could only prove in a negative sense that the theory (also held by us) namely, that these oils could only be due in part to the addition of aromatic to unsaturated hydrocarbons, is untenable.

Still, the results thus found are worth being published, inasmuch as they tend to throw some further light upon the processes incidental to high-pressure distillation. Our experiments were started with the simplest representative of the addition products of the kind described by us in this paper, Vol. 24, p. 2785, that is to say, phenylxylylethane, a by-product of the process of washing crude xylene, which, although in rather impure state, remains in the residue when distilling off xylene. By repeated fractionation it was possible to prepare a product sufficiently pure for the purposes in question. Of the substances used, about 90% boiled between 270 and 310°. The apparatus in which the dissociation was produced is the well-known distilling boiler provided with a regulating valve and constructed of wrong iron, in which it is possible to do distilling work up to 25 [fol. 761] atm, with the pressure being kept at rather constant values. In the case of xylene-styrene, the dissociation was successful even at as low a pressure as 10 atm, indeed, after some experience, it was possible to carry out the process without the formation of a coky residue, as soon as it was found that the pressure must be relieved after the gas dissociation has ceased or as soon as the pressure has decreased, whereafter the remainder of the content is continued distilling in the presence of strong air diminution.

In this manner, in a normally proceeding test with initially 10 atm, and subsequent vacuum, we obtained from 500 grams of material:

155 grams liquid distillate
295 grams solidifying distillate
10 grams — 20 liters of gas

37 grams residue free from coke.

In the solidifying portion methylanthracene and anthracene are contained in large quantities and their presence proved. By a special experiment with pure methylanthracene it could be easily shown that, when separately heated, the same liberates gas even at a pressure of 4 atm, and that it is dissociated into carbon and combustible gases containing hydrogen. This explains the observed formation of relatively large quantities of carbon in the distillation residue in a number of tests with xylene-styrene.

The liquid components of the distillate included slight quantities of phenols, a fact which indicated contamination of the raw or starting material by polymerized cumaron or its holologs, and in addition sometimes more of hydrocarbons de-coloring bromine; the remainder, apart from oils with high boiling point and starting material that had remained non-dissociated, consisted of toluene and pseudocumene apart from a slight quantity of xylene. The gas consisted of 17.1% hydrogen, the balance of hydrocarbons, especially methane.

Hence, the pressure distillation is substantially attended by two reactions, to-wit:

1. The molecule is closed into the ring:

$$C_6H_5.CH.\ C_6H_3(CH_3)_2 = C_6H_4{<}\begin{matrix}CH\\|\\>\end{matrix}C_6H_2(CH_3) - CH_4 - H_2$$

2. The molecule dissociates in the middle of the estyrene chain, while taking on hydrogen:

$$C_6H_5.\ CH.\ C_6H_3(CH_3)_2 + H_2 = C_6H_5.\ CH_3 + C_6H_3(CH_3)_2$$

[fol. 762] A very similar behavior is exhibited by dimethyldicumylmethane (see this paper, Vol. 24, 2, p. 2791) when subjected to pressure distillation. Also in this case, the dissociation proceeds in the presence of comparatively low pressure. It is true that in the first stage, with closing of the ring, hexamethylanthracene is obtained, but the latter, on account of the splitting off of further methylene groups (whence the production of olefins) results in dimethylanthracene. The latter represent the chief component of the solid separations of the distillate. But at the same time, splitting in another direction is observed. The mole-

cule breaks up, so that methylated benzine in addition to carbon are produced, in that the hydrogen set free incidental to the closure of the ring, fills up the gaps. Incidentally tetramethyl benzine will in the main be produced, but these in part due to loss of methylene groups, can be changed into xylene and toluene. Tetramethyl benzine and xylene could be separated in corresponding quantities without any difficulty.

Pressure Distillation of Rosin Oil

90% of the starting material had a boiling point ranging between 330 and 335°. The elementary analysis as well as the determination of molecular weight according to Bechmann indicated the well-known formula $C_{18}H_{28}$.

Found	C. 8893 H 10.77
Calculated	C 88.52 H 10.48

Molecular weight found 240.5 and 242.2. Calculated 244.

Both pressure and temperature had to be kept considerably higher than in the tests just described. Complete dissociation happened only at 450° and a pressure of 25 atm. For this reason formation of coke could never be avoided, the coke in some cases amounting to more than 10% of the starting material.

Another point is that the dissociation was never so smooth as in the case of phenylxelylethane, and the yield of distillate was by far lower on account of the high temperature and the great losses associated therewith due to leakage of the apparatus.

In a more or less normally proceeding process, there were obtained, from 500 grams resin oil:

105 grams liquid distillate

50 grams partially solidifying distillate

[fol. 763] 100 liters—about 80 grams gas*

141 grams residue with much coke.

---

*The gas contained in one case 8% olefins and 92% methane and homologs thereof; in another case 6% olefins, 6.2% hydrogen, and 87.8% methane and its homologs, which corresponds approximately to a weight of 0.8 gram per liter.

90% of the first distillate came over between 80 and 240°; it contained appreciable quantities of bodies discoloring bromine, it had the smell of essence of rosin, and exhibited a composition entirely resembling the latter; in other words apart from benzol hydrocarbons, especially cymene and methylated cymenes, it contained hydrocarbons richer in hydrogen resulting therefrom by hydrogenation; but paraffins and naphthenes were absent, seeing that the different fractions can be completely resinfied or sulfurated by concentrated sulfuric acid.

From the second distillate a solid hydrocarbon with high boiling point could be obtained, and the same could be dissociated by partial precipitation with picric acid into phenanthrene and methylphenanthrene. The former was obtained in the form of nice golden-yellow needles resembling the picric acid compound melting at 145°, the other in the form of crystals melting at from 90-95°, which upon analysis was found to answer the formula $C_{15}H_{12}$ with this composition:

Found	C 93.82	H 6.11
Calculated	C 93.75	H 6.25

The gas consisted of methane and hydrogen apart from slight quantities of olefins. Also in this case the reaction is evident.

Rosin oil is the dissociation product of abietic acid or its anhydrid occurring in quantities of 80% and over in colophony which in turn is probably due to oxidation of a polymeric perpene.

The rosin oil resulting therefrom, with incidental dissociation of carbonic acid and carbon monoxide, consequently is a residual product of deterpene and presumably represents a hydrated derivative of fichtelite. But pressure distillation also in this case either results in closure of the ring with incidental elimination of hydrogen and formation of methylisoprophylphenanthrene, i.e., retent, whence the isopropyl group and further also the methyl group drop out readily, or else dissociation of the two terpene fragments with re-formation of methylated and partly hydrated benzine.

[fol. 764] That rosin oil bears a close resemblance and relationship to retene had already been demonstrated by the very refined and smooth method of preparing the lat-

ter when boiling rosin oil by means of sulphur (G. P. No. 43802); the relationship with terpene has already been proved in earlier work dealing with the study of a great number of oxidation processes in which the formation of isophthalic acid, terbenic acid, and otherw was observed.

From the fact that the rosin oil exclusively phrenanthreme derivatives are obtained, it may be inferred by the way that coal tar, which apart from anthracene furnishes considerable quantities of phrenanthrene, must originate from a primary material rich in rosin. The generally held opinion that woods rich in rosin have contributed in the production and formation of hard coal, finds thus an additional support.

Now, rather obscure are the phenomena observed in connection with the pressure distillation of Russian lubricating oil.

Pressure-Distillation of "Bakunin"

The material used boiled in the range between 360 and 420°, and resulted upon combustion in

	I	II
C	87.3%	86.8%
H	12.9%	13.2%

In spite of the application of the highest admissible pressure, dissociation occurs at such a high temperature (around 450°) that to make an attempt to utilize the nature of the distillate for the purpose of determining the constitution of the molecules seemed from the outset rather hopeless. What was characteristic, however, was the larger content in olefins, especially in the fraction boiling below 200°, and the quite reliably demonstrated absence of any aromatic hydrocarbons whatever. In the main, so far as quantity is concerned, naphthenes and paraffins were present.

From 500 grams, according to temperature, from 50 to 100 liters gas, 320 grams distillate and about 50 grams of the pitch-like residue were obtained. Hence, also in this case, due to diffusion through the highly heated walls of the container and the gaskets, considerable losses were occasioned.

The gas contained 20.8% of a component absorbable by bromine, the balance being almost pure methane, apart

from a few homologs of the latter. 90% of the liquid dis- [fol. 765] tillate boiled below 280°, with a spec. gr. of 0.805. 1 gram of the crude distillate discolors 0.55 gr. bromine. After fractionation, the fractions boiling below 150° consumed about 0.75 gram bromine per cubic centimeter, while the fractions with higher boiling points consumed 0.25 gram and less. From the fractions with the highest boiling points (which in part represented unchanged lubricating oil) and from the residues, small quantities of a substance melting after purification between 202 and 205° were obtained. The lump analysis made with a fraction of the crude distillate carefully washed with sulfuric acid and boiling close to 120° resulted in figures which seemed to indicate the presence of a mixture of naphthenes and paraffins. The presence of the former was proved by treating the respective fraction with bromine and alluminum chlorid. The result in tetrabromxylene of the kind also obtained by Markownikoff from octonaphthene whose boiling point corresponds to the fraction here used. According to Thorpe and Young (see Ann. d. Chem. Vol 165, 1), in the pressure distillation of solid paraffin, substantially only liquid paraffins are obtained apart from olefins. An experiment carried out by us gave the same result insofar as we did not succeed in proving by chemical means in the remaining mixture of unattacked hydrocarbons the presence of naphthenes, after careful washing with concentrated and fuming sulfuric acid. Hence, the presence of relatively large quantities of solid paraffins in lubricating oil which might be kept in solution by the components with larger carbon contents of the same (similarly as in the case of organic salts with reference to cane sugar in molasses) seems, therefore, out of the question.

However, we have taken pains to furnish additional proofs in that respect by that the lubricating oil was repeatedly washed with large volumes of sulfuric acid, while furthermore weighed quantities of solid paraffin were dissolved therein. It was found that in the first case no paraffin was crystallized out, a thing that should have happened seeing that the sulfuric acid had removed part of the solvent; in the other case, even at 0°, almost the entire paraffins was separated out in solid form.

Also from the composition that was found and which, in conjunction with the boiling point seems to indicate something intermediate between the formulae $C_{20}H_{30}$ and $C_{25}H_{44}$:

[fol. 766] Calculated ..... C 87.08, H 12.92
Found (Average) ..... C 87.05, H 13.05

the presence of larger quantities of hydrocarbons anwering the formula $C_n H_{2n-2}$ can be inferred, as otherwise aromatic substances richer in carbon should be found in the lubricating oil, and this has so far not been possible. In the light of the above findings, it follows that lubricating oils must be regarded as a mixture of homologs of a hydrocarbon series, and which may be claimed to have by no means less a uniform chemical characteristic than in the case of resin oil and xylene-styrene and its homologs above discussed. Now, since its composition would correspond to a series having 2 hydrogen atoms less than in the case of the olefins, the assumption would not be possible that lubricating oils are polymeric olefins, a thing that furthermore is little probable in view of the fact that, upon the whole, their viscosity is lower.

Since they are furthermore saturated substances in so far as they do not add bromine, there remains nothing but the assumption, at least for the time being, that they are due to the ring closure of two or more molecules of hydrocarbons belonging to the methene or methin series. Hence, we would be dealing with bodies approximately of the composition of dihydroterpene $(C_{10}H_{18})_2$. Whether it will ever be possible to furnish positive proofs, that is to say, to accomplish the formation of such bodies, would seem doubtful to us, seeing that the method by means of pressure distillation has proved to be attended with so little success in the line of proof. The same situation holds true, by the way, of hydrogen withdrawal by other means, especially by sulfur which, as will be remembered, has contributed so much towards the determination of the constitution of resin oil. Another point is that the difficulty of procuring and still more the unstable nature of hydrocarbons belonging to the series C_nH_{2n}:2 are great obstacles to further investigation.

An attempt to produce the addition of olefins to easily procurable cyclopentadien remained without success.

In the above experiments we were aided very ably by Dr. Bruhn.

Berlin-Erkner, July 1900.

[fol. 767]

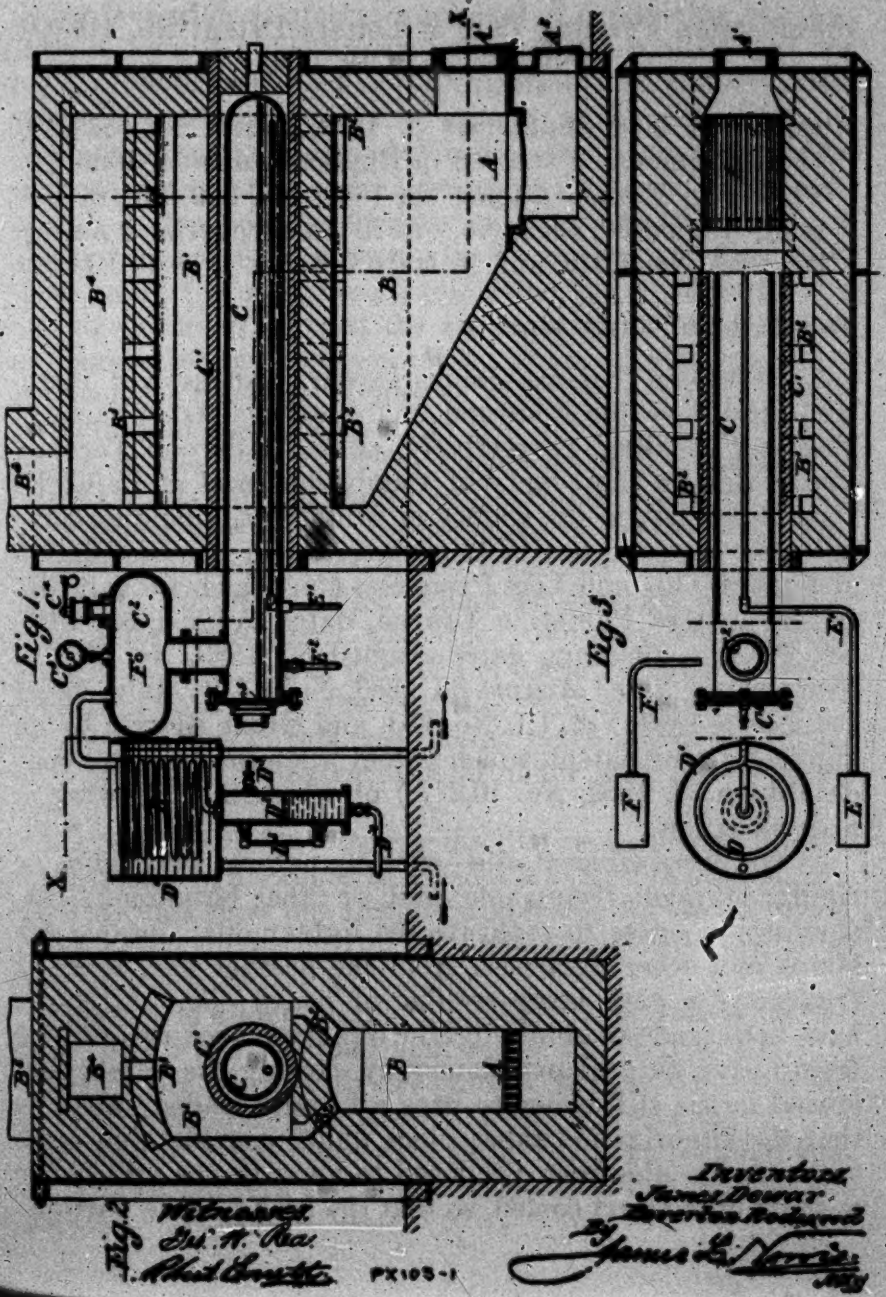
PETITIONER'S EXHIBIT 103.

(No Model.)

J. DEWAR & B. REDWOOD.

PROCESS OF DISTILLING MINERAL OILS AND LIKE PRODUCTS.

No. 419,931. Patented Jan. 21, 1890.



Witnesses:
Geo. H. Rea.
Robt. Sinnott.

Inventors,
James Dewar.
Boverton Redwood
By James L. Norris
Atty

PX103-1

[fol. 768] United States Patent Office

James Dewar, of Cambridge, County of Cambridge, and Boverton Redwood, of Finchley, County of Middlesex, England

Process of Distilling Mineral Oils and Like Products

Specification Forming Part of Letters Patent No. 419,931, Dated January 21, 1890

Application filed September 3, 1889, Serial No. 322,856. (No specimens. Patented in England June 24, 1889, No. 10,277; in France August 30, 1889, No. 200,495; in Belgium August 30, 1889, No. 87,570; in Switzerland August 30, 1889, No. 1,339, and in Italy October 1, 1889, LI, 233.

To all whom it may concern:

Be it known that we, James Dewar, professor of chemistry, and Boverton Redwood, analytical chemist, citizens of England, residing, respectively, at No. 1 Scroop Terrace, Cambridge, in the county of Cambridge, and at Ballard's Lane, Finchley, in the county of Middlesex, England, have invented new and useful Improvements in the Distillation of Mineral Oils and Like Products, (for which we have obtained Letters Patent in France, dated August 30, 1889, No. 200,495; Belgium, dated August 30, 1889, No. 87,570; Switzerland, dated August 30, 1889, No. 1,339; Italy, dated October 1, 1889, Vol. LI, No. 233, and Great Britain by an application for patent, which patent when granted will bear date June 24, 1889, No. 10,277,) of which the following is a specification.

In distilling mineral oils—such as natural petroleum or similar oil made from shale, coal, or other bituminous substances—in order to separate the lighter oils, suitable for lamps and other purposes, from the heavier oils, there is frequently a very large residue of heavy oils. Attempts have been made to obtain lighter oils from such residues or from heavy natural petroleums by causing the vapor generated in the still-boiler to pass a heavily-loaded valve, so that the vaporization takes place under considerable pressure. It has also been proposed to arrange the still-boiler with its upper part cooled, so that the best volatile portions

of the vapor may become more or less condensed and fall back into the hot liquid below, this mode of operating being commonly termed "cracking." Both these methods are objectionable, the former on account of the irregularity of the distillation and the latter on account of the waste of heat in conducting the cracking process and the slowness and insufficiency of the results.

Our invention relates to a method of conducting the distillation by a suitable apparatus in such a manner that we get the benefit of regular vaporization and condensation under high pressure, and that we may at the same time get such advantage as can be obtained from cracking. For this purpose we arrange a suitable boiler or retort and a condenser in free communication with one another without interposing any valve between them; but we provide a regulated outlet for condensed liquid from the condenser. We charge and keep charged the space in the boiler or retort and condenser that is not occupied by liquid with gas under considerable pressure, it may be with air or it may be with carbonic-acid gas or other gas that cannot act chemically on the matter treated. The distillation and condensation being thus conducted under considerable pressure, which can be regulated at will, we obtain from the heavy residue a quantity of more or less light oil suitable for illuminating and other purposes, which cannot be obtained by distillation under atmospheric pressure. We may also arrange the still-head or upper part of the boiler or retort so as to operate according to the cracking method above referred to, the cracking in this case taking place under high pressure instead of being carried on under atmospheric pressure.

The apparatus for effecting distillation in the manner described may be arranged in various ways. The accompanying drawings show one form of apparatus for this purpose, which is the subject-matter of a patent application of even date herewith, Serial No. 322,857.

Figure 1 is a longitudinal and Fig. 2 is a transverse section. Fig. 3 is a sectional plan on the line X X of Fig. 1.

A is a fire-place, with fire-door A′ and ash-pit door A², suited for regulating admission of air as required.

Instead of a fire-place with grate for burning solid fuel, any known burners for liquid or gaseous fuel may be employed.

Above the combustion-chamber B is placed a metal retort C, which is inclosed within a refractory casing C′ to protect the metal from excessive local heating. The incased retort is situated in a heating-chamber B′, into which the hot products of combustion ascend by side ports B^2 and from [fol. 769] which they pass by central ports B^3 into a flue B^4, communicating with a chimney B^5. The front part of the retort C communicates freely with a still-head C^2, provided with a pressure-gage C^3 and safety-valve C^4. The exposed end of the retort C is closed by a readily-removable cover C^5, provided with a glass gage to show the level of the liquid in the retort.

D is a pipe-coil situated in a tank D′, in which circulation of water is maintained. The upper end of the coil D communicates by a pipe with the still-head C^2 and its lower end opens into a hollow column D^2, which is provided with a glass gage D^3 and has at the bottom an outlet-pipe D^4, furnished with a stop-cock or valve.

E is a pump for forcing the oil to be treated by a pipe E′ into the retort C, this pipe preferably extending nearly to the farther end of the retort. By another pipe E^2, furnished with a cock or valve, the contents of the retort can be drawn off, or this pipe may communicate with a second retort, which in like manner may be connected with a third, so as to form a series of any required number.

F is an air-compressing pump, by which air or suitable gas is forced by a pipe F′ into the still-head C^2, or it might be into any other part of the apparatus which is in communication with the still-head. The retort C being partly charged with oil by the pump E, and the spaces in the retort C in the still-head C^2 and in the condensing-coil D and column D^2 being charged with air or gas to the desired pressure, the retort is heated, vaporizing the oil under pressure. The oil-vapor is condensed in passing through the coil D and the liquid distillate collects in the column D^2, and is drawn off either continuously or intermittently into suitable receptacles, in which such gas as may be dissolved in the liquid is liberated and can be collected.

By a pipe and cock or a suitably-loaded safety-valve D^5 gas may be withdrawn from the space above the liquid in the column D^2.

Although we have shown one retort and condenser, there may be several sets of these in communication with the oil

and gas pumps or with each other, suitable cocks or valves being provided in the communicating pipes, so that the several retorts may be worked simultaneously or in rotation. From time to time the cover C^6 of the retort may be removed to clear out residue. During the distillation such of the vapor as may be condensed in the still-head C^2, or such liquid as may prime up into the still-head, flows back into the body of liquid in the retort. By regulating the heat and pressure to which the retort is subjected the character of the distillate may be varied, and thus oils more or less light can be obtained to suit various uses. Also, the proportions of the parts may be varied, and, if necessary, means of cooling may be applied to the still-head C^2.

Having thus described the nature of our invention and the manner of carrying the same into effect, we claim—

The herein-described method of distilling mineral oils and like products, which consists in both vaporizing them and condensing the generated vapor under a regulated pressure of air or gas, substantially as specified.

In testimony whereof we have signed our names to this specification, in the presence of two subscribing witnesses, this 13th day of August, A. D. 1889.

James Dewar, Boverton Redwood.

Witnesses: Oliver Imray, Patent Agent. 28 Southampton Buildings, London, W. C. Jno. P. M. Millard, Clerk to Messrs. Abel & Imray, Consulting Engineers and Patent Agents, 28 Southampton Buildings, London, W. C.

[fol. 770]

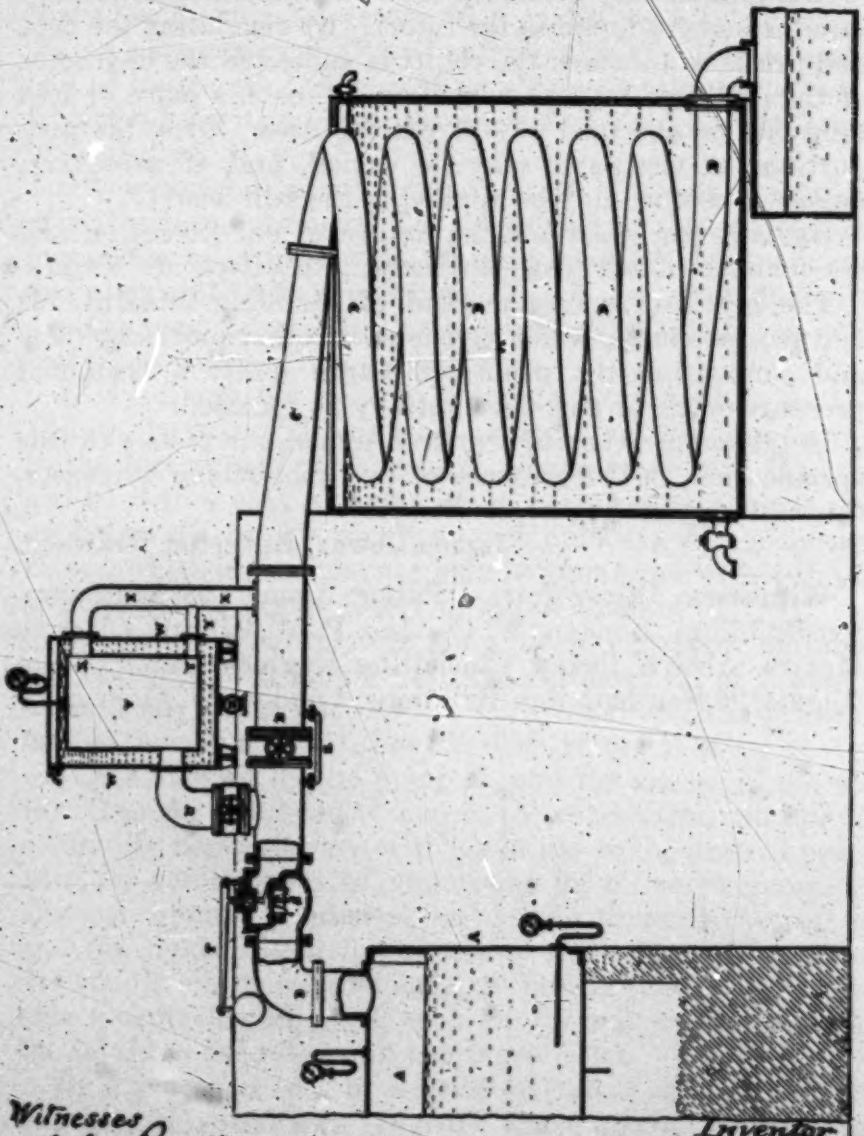
PETITIONER'S EXHIBIT 104

(No Model.)

J. LAING.

APPARATUS FOR THE DESTRUCTIVE DISTILLATION OF MINERAL OILS.

No. 471,291. Patented Mar. 22, 1892.



Witnesses
John Revell
George Baumann

Inventor
John Laing
by his attorneys
Munn and Munn

PX 104-1

[fol. 771] United States Patent Office

John Laing, of Edinburgh, Scotland

Apparatus for Destructive Distillation of Mineral Oils

Specification Forming Part of Letters Patent No. 471,291, Dated March 22, 1892

Application filed May 29, 1891. Serial No. 394,483. (No model.)

To all whom it may concern:

Be it known that I, John Laing, a subject of the Queen of Great Britain and Ireland, and a resident of Edinburgh, in the county of Mid-Lothian, Scotland, have invented certain Improvements in Apparatus for Destructive Distillation of Mineral Oils, of which the following is a specification.

My said invention has for its object the treatment of mineral oils by destructive distillation under high pressure in order to convert them into lighter products.

In carrying out my invention I apply a regulation or escape valve to the outlet from the oil-still and load it to the required pressure at which the oil is to be distilled. As the oil, gases, or vapors exceed the pressure to which the valve is loaded, they pass through the valve into a large iron vessel, which I term the "relief-tank," as it relieves the pressure by distributing it over a large area. An outlet-pipe from the relief-tank is connected to a condensing-worm, which has a free terminal outlet. The relief-tank may be placed in an outer vessel and be submerged in cold water made to flow continuously through the vessel, the relief-tank being thereby made to act as a condenser. The relative aggregate capacity of the condensing-worm and relief-tank, when the latter is used as a condenser, should be such that all the oil, gases, or vapors will be condensed and the distillate will run off at atmospheric pressure, and in order that my said invention and the manner of performing the same may be properly understood, I hereunto append a sheet of explanatory drawings, to be hereinafter referred to, and representing by way of example, a modification of my improved apparatus.

The figure on the sheet of drawings is a longitudinal vertical section, showing a part of the primary oil-still A and the apparatus connected therewith. This oil-still A

may be constructed and may operate like what is described in the specification filed with my application for United States patent on January 8, 1891, Serial No. 377,121, in which case the part shown will be the last compartment of the still, the oil having undergone successive stages of destructive distillation in the several compartments; or the still A may be of ordinary construction. The gas or vapor evolved in the still A passes off by a pipe B, a continuation, C of which leads to a condensing-worm D. A stop-valve E is interposed between the parts B and C, and in the part B there is arranged a valve S, loaded by means of a weighted lever T, acting on the valve-spindle, which extends through a stuffing-box. Between the valves S and E a branch pipe U communicates with a relief tank or vessel V, which is placed inside of an outer vessel W, having cold water flowing continuously through it. The relief-tank V communicates by a pipe X, connected to its upper end with the pipe C, leading to the condensing-worm D, and there is also a smaller pipe Y, connected to the bottom of the relief-tank, to lead off condensed oil either to the pipe C and condensing-worm, as shown, or it might be to a separate receiver. A small inverted siphon-pipe Z is fitted under the valve E to allow any oil which may condense in the part of the pipe between the valves E and S to pass on to the condensing-worm D. A suitable pressure to which to load the valve E will depend upon the kind of oil operated on and will be best ascertained by trial. It may, however, be stated, by way of example, that I believe eighty pounds per square inch will be found a suitable pressure for operating on a mineral oil of .970 specific gravity in order to obtain therefrom an oil of about .700 specific gravity.

What I claim as my invention is—

The combination, with a still for the destructive distillation of mineral oils, of a loaded outlet-valve and a relief-tank interposed between the said outlet-valve and an ordinary condenser, the said relief-tank being used more or less as a condenser, substantially as and for the purposes herein set forth.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

John Laing.

Witnesses: Edmund Hunt, David Ferguson.

[fol. 772]

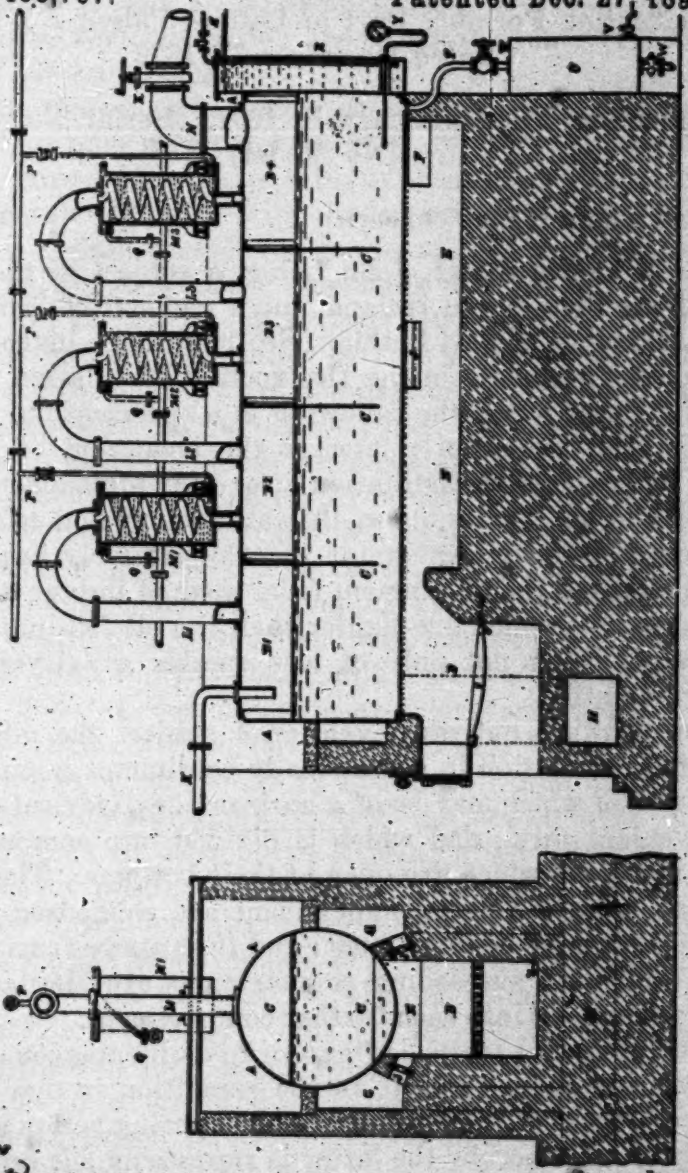
PETITIONER'S EXHIBIT 105

(No Model.)

J. LAING.

DESTRUCTIVE DISTILLATION OF MINERAL OILS.

No. 488,767. Patented Dec. 27, 1892.



Witnesses
George Baumann
John Revell

Inventor
John Laing
By his attorneys
Howson and Howson

PX.105-1

[fol. 773] United States Patent Office

John Laing, of Edinburgh, Scotland

Destructive Distillation of Mineral Oils

Specification Forming Part of Letters Patent No. 488,767, Dated December 27, 1892

Application Filed January 8, 1891. Serial No. 377,121. (No Model)

To all whom it may concern:

Be it known that I, John Laing, a subject of the Queen of Great Britain and Ireland, and a resident of Edinburgh, in the county of Mid-Lothian, Scotland, have invented certain Improvements in the Destructive Distillation of Mineral Oils, of which the following is a specification.

My said invention relates to the treatment of mineral oils by destructive distillation at or near atmospheric pressure, and has for its object the satisfactory and economical decomposition or conversion of comparatively heavy mineral oils, and the obtainment from them of lighter products. That is, oils which are lighter than the oil fed into the apparatus, being not only of less specific gravity but also more volatile.

In carrying out my invention I subject the oils to repeated distillation in a practically continuous manner, in a boiler still which may be of a horizontal cylindrical or other convenient form, and which is divided into compartments by partitions which are open at their bottoms. The vapors rising from the first compartment are condensed and led into the second compartment; and the vapors from the second and each succeeding compartment are similarly condensed and led into each further compartment.

The important feature of practically advantageous novelty in my invention consists in the repetition in one and the same process of the volatilizing or vaporing action upon the body of oil, whereby the latter is repeatedly slit up and the lighter portions completely detached or carried off. Besides this the process carries with it the advantages of rapidity of operation and uniformity of product.

In order that my said invention and the manner of performing the same may be properly understood, I hereunto append a sheet of explanatory drawings to be hereinafter referred to, and representing by way of example a modification of my improved apparatus.

Figures, 1, and 2, of the drawings are respectively a transverse vertical section and a longitudinal vertical section of the apparatus.

In the drawings the same reference letters are used to mark the same or like parts wherever they are repeated, two or more similar parts being in some cases distinguished by numerals combined with the letters.

The distilling vessel is in the form of a horizontal cylindrical boiler, A, which is externally divided into compartments, B′, B², B³, B⁴, by vertical partitions, C, which are open at the bottom to allow of free communication of the liquid oil through all the compartments, the openings or spaces beneath the partitions being, by preference, large enough to allow of access for cleaning purposes to all the compartments. The boiler, A, is set in brickwork and is heated by means of any suitable fuel in a furnace, D, at one end beneath the first compartment, B′, the fire gases proceeding along a flue, E, extending under the middle of the boiler to the other end, and there communicating by side ports, F, with return flues, G, at the sides of the boiler. The return flues, G, communicate at their front ends, by descending flues, with a horizontal flue, H, which may pass under a number of boilers to a chimney. Additional ports, J, form communications between the bottom flue, E, and the side flues, G, these ports, J, being fitted with adjustable dampers by means of which the heat acting on the after parts of the boiler may be more or less moderated if required, the fire gases tending to take the nearer route to the chimney through the ports, J, when their dampers are open. The end ports, F, may also be fitted with dampers for closing them more or less if found desirable.

The oil to be operated on is, ordinarily, supplied to the first compartment, B′, by a pipe, K, and the vapors or gases evolved in that compartment pass by a pipe, L′, into the worm of a condenser, M′, the condensed products dropping into the second boiler compartment, B². In like manner the vapors or gases evolved in the other compartments, B², B³,

pass by pipes, L^2, L^3, into the next compartment, B^3, B^4. There may be more or fewer than the four compartments shown if found desirable. From the compartment, B^4, or the last of the series, the vapors or gases pass off by a pipe, N, to any suitable condenser or condensers.

The condensers, M, are supplied by a main and branch [fol. 774] pipes, P, provided with stopcocks, with cold water, which enters at their lower ends, the heated water passing off from their upper ends by branch pipes and a main pipe, Q. As I believe it will in some cases be desirable to cool the back end of the boiler, that is, the last compartment, B^4, I provide, there, a casing, R, with pipes, S, for supplying cold water and leading off the heated water. And at the bottom of the back end of the boiler I provide a pipe, T, for drawing off the unvolatilized residue from the oil. In some cases the residue although liquid while hot, hardens on cooling into a pitch of good quality; and the operation of the apparatus may be varied and regulated in a manner to obtain the residue or pitch in what may be considered to be the best condition. The residue pipe, T, communicates with a receiver, U, fitted with a cock, V, for drawing off a test sample, and also with a pipe for conveying the residue to a more distant receptacle, the pipes, T, and W, being both fitted with stopcocks.

When distilling mineral oil according to my improved system no steam unless superheated is on any account to be let into or used in the still boiler as it would prevent the efficient breaking up or decomposition of the oil. If the still is being fed continuously, or indeed in any case, great care must be taken to have the oil "dry," that is, quite free from water. In each succeeding compartment of the still more and more of the lighter oil is obtained; and the heat applied to the still should be regulated so that what acts on the last compartment, B^4, may be just sufficient to volatilize the lighter oil and thus separate it from the heavier remaining liquid. I apply a stricture valve, X, to the final delivery pipe or swan-neck, N, which conveys the vaporized oil from the last compartment to the condensers, for the purpose of by its means regulating the rate of delivery by reducing or increasing the opening through the swan-neck.

In order to assist the regulating of the heat applied to the last compartment, B^4, I have a pyrometer, Y, applied to that compartment with its inner end immersed in the liquid oil; and when the proper temperature for that compartment has been determined by trials in the case of any particular kind of mineral oil, the heat can thereafter be suitably regulated by aid of the pyrometer.

Pipes may be provided for supplying fresh or cold oil to any of the compartments as well as to the first, such arrangement affording additional means for regulating the effective temperatures within the apparatus. Suitable pressure gages and thermometers or pyrometers may be fitted to the apparatus wherever it may be thought desirable. The actual internal pressure may be varied to a small extent by means of the stricture valve, X, in the end outlet or swan-neck, N, and by suitably regulating the action of the condensers or otherwise, it not being essential to my process to restrict the internal pressure exactly to atmospheric pressure as it may exceed that pressure to a small extent, say not more than ten pounds on the square inch, or it may be less without injurious results.

What I claim as my invention is:

An improved process for treating heavy mineral oils to obtain lighter oils, the said process consisting in distilling the oil from a series of compartments or vessels, the liquid in all of which is in communication, and passing the volatilized matters through condensers from each compartment or vessel to the next in order and from the last to ordinary condensers, the condensed products from each condenser but the last being led to the body of oil under treatment in the successive compartments, substantially as hereinbefore described.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

John Laing.

Witnesses: Edmund Hunt, David Ferguson.

[fol. 775] PETITIONER'S EXHIBIT No. 106

Transactions of the Royal Scottish Society of Arts

Vol. XIII

(Seal the Royal Scottish Society of Arts)

Inst. 1821. Incor. 1841

Edinburgh:

Printed for the Society by Neill and Company.

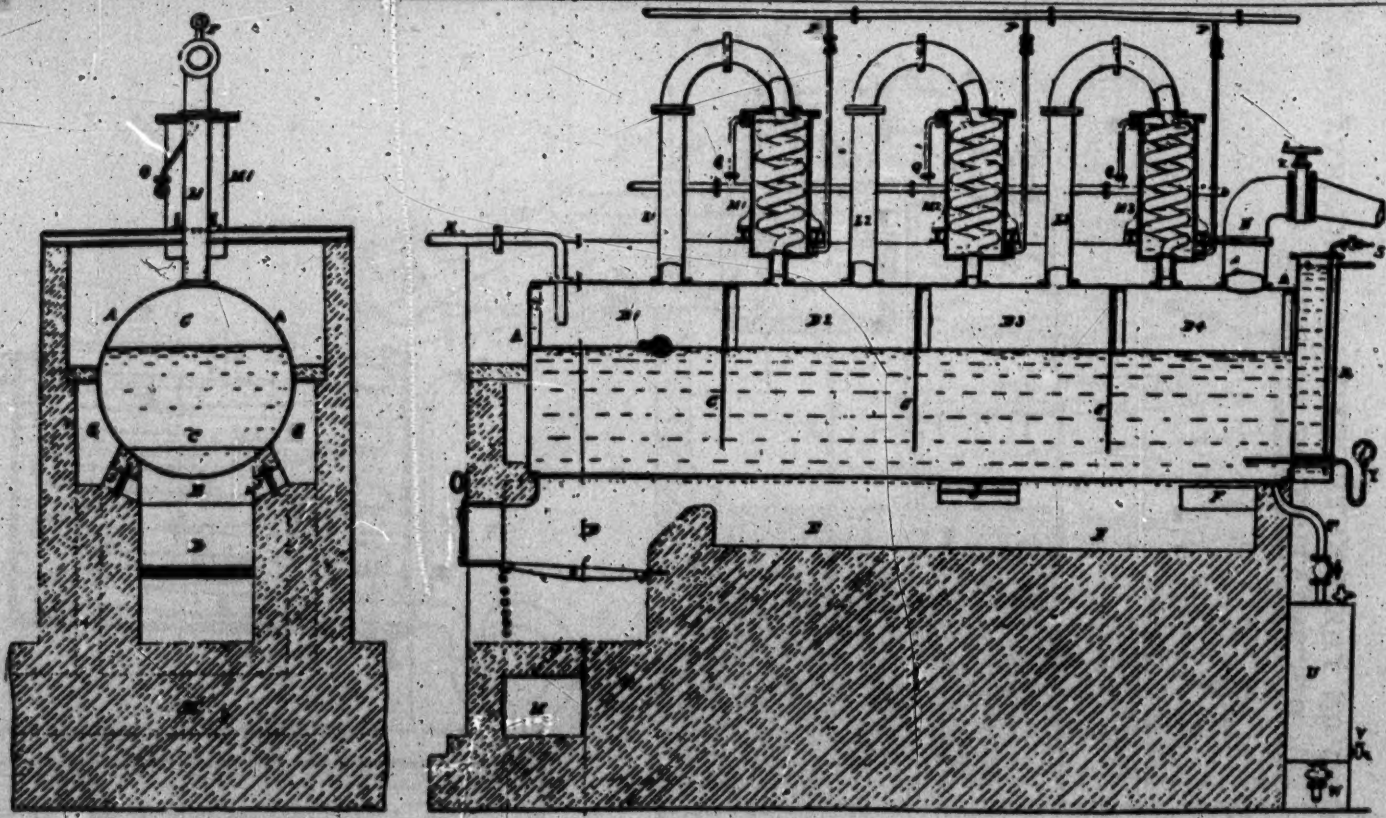
1894

71477

(Pages 151 to 163)

FIG 1. FIG 2.

AING ON THE DESTRUCTIVE & CONSERVATIVE DISTILLATION OF MINERAL OILS.



[fol. 776]

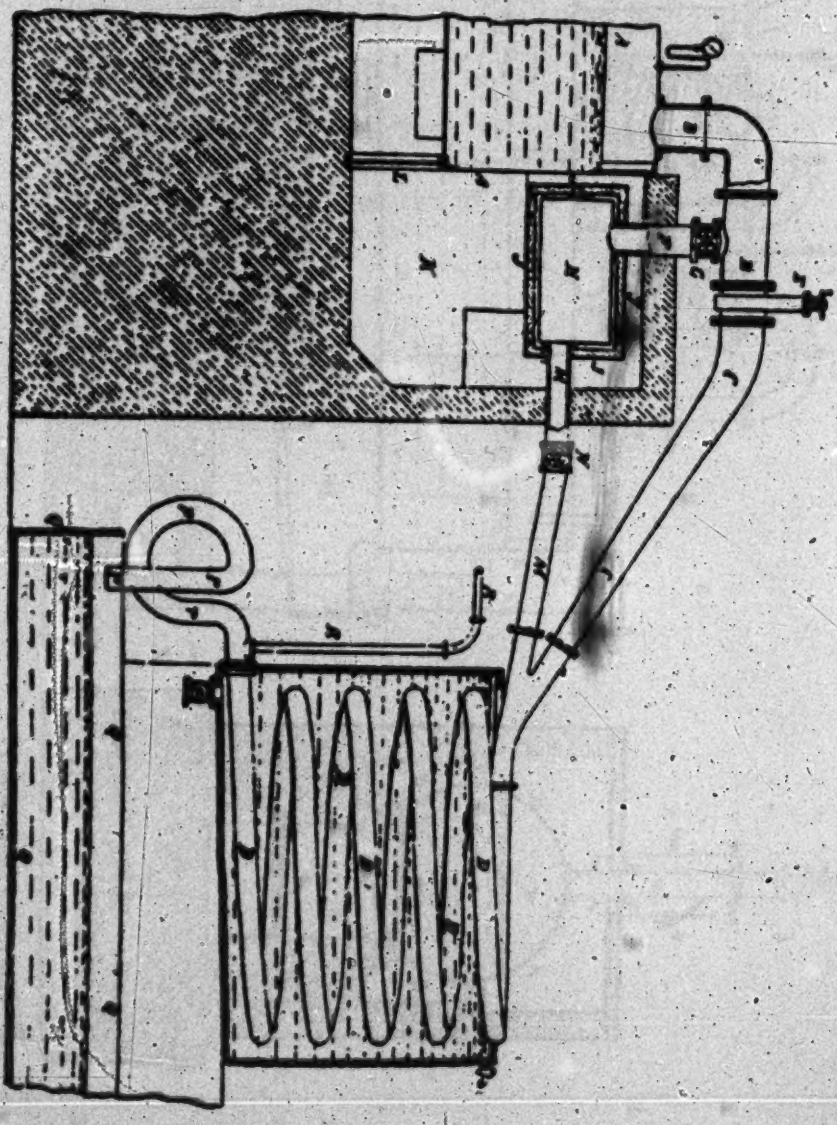
3995

PX164-2 Royal Scottish Society of Arts Transactions Vol XIII, Plate 1

SCALE.

Royal Scottish Society of Arts. Transactions Vol. XII. Plate 2

LAING ON THE DESTRUCTIVE & CONSERVATIVE DISTILLATION OF MINERAL OILS.

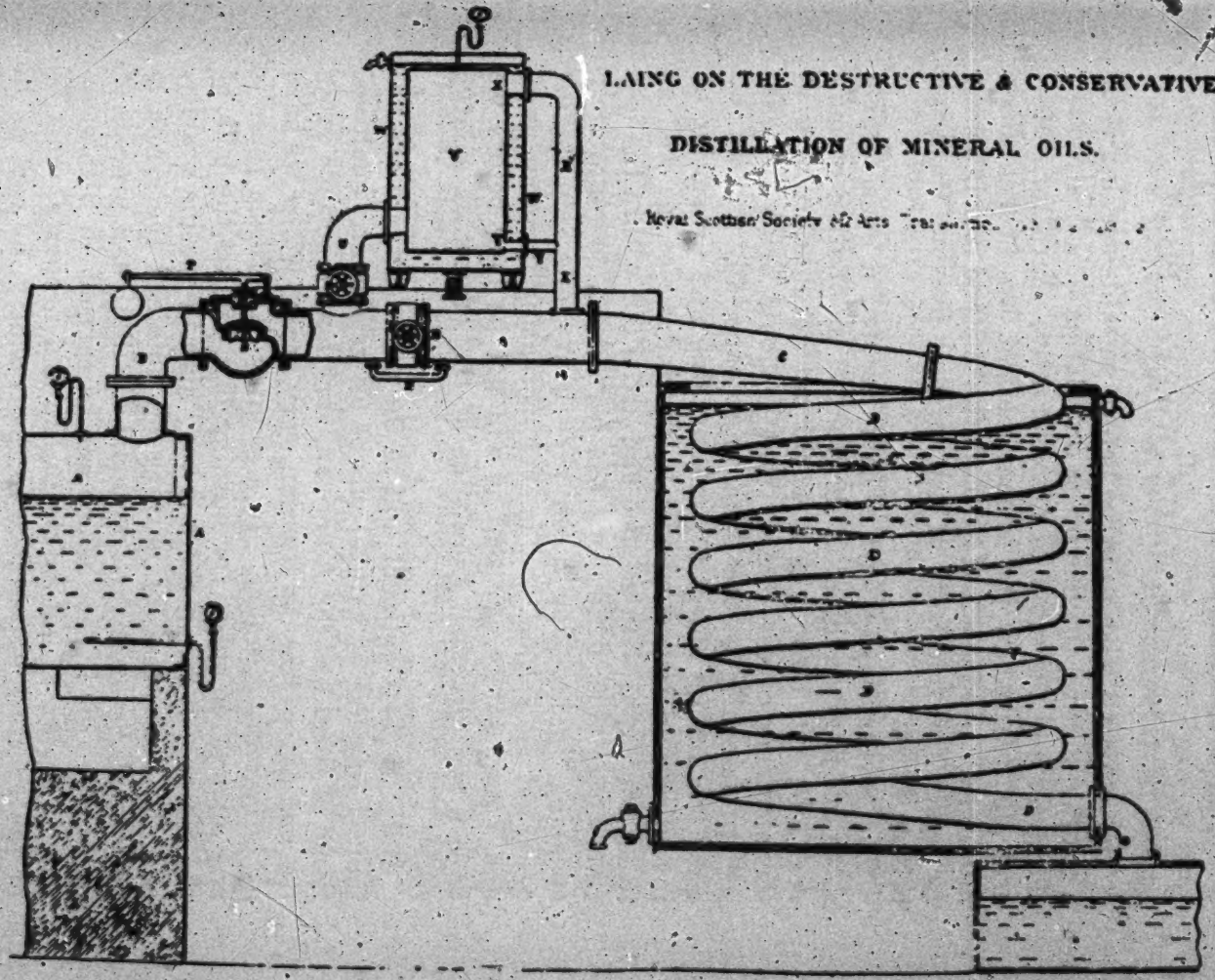


LAING ON THE DESTRUCTIVE & CONSERVATIVE

DISTILLATION OF MINERAL OILS.

Royal Scottish Society of Arts Transactions

[fol. 778]



PX 106-4

3997

[fol. 779] On Destructive and Conservative Distillations of Mineral Oils and Their Molecular Condition

By John Laing, F.I.C.* (With Four Plates)

The subject I wish to bring before you this evening is of a twofold nature, the one being distillation of a destructive character and the other of a conservative character. Mineral oils, treated by the former method, are broken down into lighter products, but by the latter method it is intended to retain the full body of the oil and prevent its being broken down.

For several years past I have devoted a considerable attention to the subject of destructive distillation of mineral oils, and I thought it would not be uninteresting to the members of the Society that I should bring the subject prominently before them, more especially as this Society has for its object the encouraging and promoting of invention and improvements in our industries, as well as in all connected with science and art. Till within the last fews years very little work has been done, comparatively speaking, in breaking down very heavy oils into lighter ones; but the subject now is ever increasing in importance, and I may safely say that it will not be long before we have a fair practical knowledge of the subject on a large scale.

Both on the Continent and in the colonies there are unlimited supplies of natural oils of all grades and qualities. Some of them like the American, very low in specific gravity, and others like the Russian, very heavy, whilst we have all intermediate grades. In a country like Russia there is any amount of outlet for burning oils, and as the bulk of the natural oil found there is very high in specific gravity, and the percentage of burning oil obtained therefrom is very small by ordinary fractional distillation, a process of destructive distillation which can be carried on with economy in working, and safety to life and property, must be of the greatest importance to that country, as well as to others similarly placed, and every day brings the demand for such a process more prominently to the front.

When mineral oil is being manufactrued, as in this country from shale, it is of the utmost importance that all

*Read before the Society, 14th December 1891.

vapours should be removed from the retort as soon as formed, and that removal should be conducted at as low a temperature as possible, for, if the gases have a long [fol. 780] travel through a very high temperature before they leave the retort, they get split up and degraded to a wonderful extent, the high melting-point paraffins get reduced, the low melting-point paraffins get split up into liquid hydrocarbons; the heavy lubricating oils get degraded into those of less viscosity, and what would form the burning oil portion gets split up into naphtha and permanent gas. I will now give you an illustration of this breaking down.

In my various experiments I was very much struck with the behaviour of certain oils, and also of the same oil under treatment of refining; for instance, I found I could not get the same results from one individual crude oil when distilled under slightly different conditions in its various fractions. For example, I found that in distilling, say 20,000 grain measures in 5 per cent. fractions in my usual still, I got certain results; but if I took 5000 grains of the same oil and distilled that quantity under the same conditions in the same still, and took it off in 5 per cent. fractions, on comparing the fractions in both cases did not get them to agree, the oil in the latter case being very much split up. Taking another 5000 grains of the same oil, and distilling it in a smaller still, the capacity of which was one-fourth of that of the large one, I got the fractions to correspond more nearly; the setting points, viscosity, and gravity of the various fractions were nearly the same as the distillate in the larger still.

I tried another experiment with the larger still, in the one instance, using wide delivery tubes, and in the next distillation I used very narrow or small bore tubes, and I found I got a degraded oil in this second distillate, which corresponded, in a degree, with the distillate of the small quantity in the large still. I then fitted up another set of delivery tubes, having a stop-cock arrangement so that I could regulate the outflow of the gases from the still, and I found that I could obtain results very different from anything I had yet got, according as I left a smaller or larger aperture for the gases to pass. I tried yet another experiment in a larger still with wide delivery tubes, but in this case I fed the still at the same rate as the distillate came off; in other words, I kept the still, as nearly as possible,

at the same level, and I found that I got the best results by far of any of my former distillates. The smell was sweeter, gravity higher, paraffin of high melting point, greater in quantity, and the viscosity of the lubricating oil much higher, and the corresponding loss was less.

[fol. 781] The conclusions I came to were that radiant heat was the cause of the degraded condition of the resulting oils, and that also pressure might assist this breaking down, for when I restrained the flow of vapours from the still it naturally put a back pressure on the still. Pressure, pure and simple, without distilling heat, does not affect the oil. You may put on a pressure of 200 lbs. per square inch in your still, and keep it at that for twenty-four hours, and your oil will be unchanged. If you take a high boiling point oil, say over 500° F., and heat up the contents of your still within its distilling point, ever so little, say to 500° F., and let it remain locked up under 150 lb. pressure per square inch, so that no vapours can possibly escape, and leave it so for twelve hours and let it cool down, you will find that the oil has changed very little indeed; the invisible molecular energy caused by the applied heat had not reached that point which was necessary to force the molecules so far apart as to break down the compound molecules.

What action, then, has pressure on an oil when distilled under its influence? It is simply this:—It raises the boiling point, and thus necessitates the entrance of more heat into the oil for its evaporation, and the energy of this extra heat assists in breaking down the cohesive attraction of the compound molecules of which the oil is built up, and at the same time it keeps the gases in the still longer under the action of the radiant heat from the sides of the still above the level of the liquid inside; and as these sides, or portion of the still, allow more heat to enter the still than the bottom portion covered with a deep layer of oil, which is a bad conductor of heat, the gases held there by the pressure are constantly being split up, and lighter products formed. It is just a question of time; if you fire heavily, and bring away the vapours as fast as formed, you will get a heavier distillate than if you fired slow and kept your heat just hight enough to evaporate your oil slowly. If you keep these vapours a lengthened period in contact with the upper portion of the still, the radiant heat will soon split them up,

and a lighter distillate will be the result. If you take a works-still running heavy oil and paraffin, and for some reason or other the distillation had to be stopped and the fire drawn, when you again fire up and commence distilling you will not get the same products at start as you left off running at, when the still was damped down, you will always get light spirit or naphtha at the start, and all the distillate to the end will be of degraded character. Your [fol. 782] solid paraffins have suffered, and the viscosity of your lubricating oil has got thinned down considerably. This is partly due to the oil vapours or compound molecules remaining in contact with the hot sides of the still above the liquid portion, and there getting broken down, falling back into the still, and getting condensed, are ready to come off at a lower heat when the fire is again put on, and yield a product of lighter specific gravity. It is upon this principle that "cracking stills" at present in use are worked. The method employed is to have a high upright still, and conduct the distillation so that the heavier vapours rising up in the still will fall back again, and get condensed and redistilled or evaporated. Of course, no steam must be employed in this distillation, else it would carry over the vapours from the still and prevent their remaining long enough to get broken down. This method has never been considered very satisfactory; the distillation is extremely slow, and large quantities of the lighter vapours get converted into permanent gas. What does all this point to? It shows us that there is a limit to which we ought to allow our stills to be fired when working for heavy oils. When distilling for lubricating oils, get your gases out of your still as fast as possible; arrange your flues connected with the furnace so that the top portion of your boiler still is protected by being, to a certain extent, shut off from the hot gases from the combustion chamber. You will thus minimise the area where excessive radiant heat would do the most harm to the oil vapours; on the other hand, you must not have your still top too cold, as it would act, in a degree, as a condenser, and the heavier vapours falling back into the still would get split up by being re-evaporated. Have as free an outlet as possible from the still, and that not too high from the boiler top. I would strongly recommend an exhausting arrangement be fitted to each still for

"heavy oils and paraffin," so that the vapours would be more quickly removed and thus a lower temperature would be required to distil the oil than by the present method of distilling. Various opinions have been expressed as to the molecular condition of mineral oils, but none of them have been satisfactory to my mind. My own opinion is that mineral oils are made up of compound molecules of various sizes, and according as these compound molecules are large or small, so is the oil heavy or light, and it is the breaking down of these compound molecules into compound molecules of a smaller size which constitutes what is technically [fol. 783] known as the "cracking" of oils. (I will have a few words to say on that subject further on.) The oftener you distil a mineral oil you make it the lighter, and although you may begin with a heavy oil your first fractions in distillation will always be comparatively lighter than the fractions which built it up; and if you go on distilling this oil, over and over again, and so breaking it down, you will gradually come to very light material, which soon gets split up into permanent gas, and all you have left is a little carbon at the bottom of your still. There has always been a difficulty in obtaining a distillate of uniformly low specific gravity throughout, without entailing too great a loss through permanent gas, and it is greatly to overcome this difficulty that I have devised the apparatus before you. By referring to the diagrams you will see the internal arrangement of the same.

It consists of a divided boiler, whose compartments do not reach the bottom. This allows a free way throughout for its contents. Thus, the still when first charged will stand with all its compartments at the same level with oil. On the top of the still is a series of condensers, arranged so that the gases from the first compartment pass over, get condensed, and fall into the second compartment; then the gases from the second compartment pass over, get condensed, and fall into the third compartment, and so on to end of the still, where they finally pass over by the swan neck leading to the main condenser in connection with the general receiving tank. In using this apparatus, the greatest heat is to be applied to the end compartment furtherest from the swan neck, and it is tapered off gradually towards the opposite end. Some may be inclined to think that because there is a freeway all along the bottom of the still,

that the contents will heat up uniformly en masse, but this is not the case; heat currents have always an upward tendency—never a transverse one from their first source—and as you have a graduated heat under the still, so each compartment has a corresponding difference in temperature.

[fol. 784] I will show you this by a very simple experiment. Here is a glass tube bent so that one leg rises from a lower level than the other, i. e., the two upright legs rise from an oblique base; in other words, the legs are parallel, but they are not at right angles with the base. Fill this tube three-quarters full of water, and of course it will stand at the same level in both legs; but now let us apply heat to the highest point of the base, and you will find that the water will actually boil in that leg while the other remains comparatively cool; not only so, but you will find that the water has increased in bulk in that boiling leg. If you now apply the heat to the opposite end of base, keeping the lamp just sufficiently inwards to clear the upright leg, you will find that the heat currents will pass upwards along the base, and up the far off leg, rather than take to the nearer one, simply because they would have to force themselves downwards to arrive at the nearer leg—the natural tendency being upwards. We are accustomed to say that "water gains its own level." We ought to qualify that statement by saying "water of uniform temperature gains its own level."

Now let us follow what takes place when breaking down an oil in the form of still before you. I have already pointed out that the oftener you distil a mineral oil you make it the lighter. Well, the oil in the first compartment boils first, the vapours pass over, get condensed, and fall into the second compartment. This oil, which has now fallen into the second compartment, is lighter than the body

of the original oil in first compartment, and hence it requires less heat to reevaporate it; it here meets with that less heat, and it is again redistilled into the third compartment, always getting the lighter at each distillation into each succeeding compartment, till finally it leaves the still. If you wish to bring off an oil of uniform specific gravity, you only require to keep your finishing compartment at a corresponding steady temperature. For instance, if you wish an oil whose boiling point is 250° F., you must have your last compartment kept steady at that temperature, and no oil can possibly come over whose boiling point is higher. In order to better regulate the temperature of this last compartment, I have arranged a water jacket attached to it, with an inlet for cold water at the bottom, and an outlet for the hot water at the top; the more cold water you run through this jacket will necessarily keep the end compartment the lower in temperature, and by this means you [fol. 785] have a power of regulating the distillate to almost any gravity you want. If you try to overfine, you only increase the speed of the distillation into itself, and the cold oil constantly running from the condensers into the still guards it from harm. The still can be fed continuously, and I have made provision for the removal of residues in their most valuable form. In some cases, as in Russian oils, the unvolatilised residue, although liquid whilst hot, hardens on cooling into a pitch of first-rate quality, and in order to arrive at the proper point at which this can be obtained in the best condition, I have arranged a sampling vessel by which a small quantity can be run off, at any time, from the still bottom with perfect safety, and examined from time to time before running the bulk to the pitch-pit or tank. (A working model is before you on the table.)

Radiant Heat

Is a very powerful agent in breaking down oil vapours (see Plate No. 2), and if properly applied can be used with advantage. I have devised a method for its use, so that by simply passing the gases as they come from the still through a superheater exposing a large area of heated surface for the gases to pass over, they will readily get broken down and yield a lighter distillate according to the area,

the temperature of the superheater, and the length of time the gases are in contact with it. The diagram explains the arrangement, and shows the connections from still to condenser, and also flue arrangements for the regulation of the heat.

The syphon trap at the end of the condenser will always ensure an oil-seal, and prevent any atmospheric air from passing to the superheater; this may be quite unnecessary, but I use it as a protective measure. It also shows arrangement for connecting the still with a vacuum pump; the discharge end of syphon would have to be lengthened, and dipped into the oil according to the amount of vacuum to be balanced.

Distilling under Pressure

Is another method by which this breaking down can be accomplished (see Plate No. 3). Two methods have been employed to do this, but both of them carry with them such great defects that little has ever been done with them. One of these methods was to place the pressure valve direct on the swan neck from the still, and connect it direct to the condenser; but the vapours, under pressure, as they escaped [fol. 786] from the still, rushed with so great a force through the condenser that a very large quantity escaped into the air uncondensed—this meant loss and risk from fire.

The other method was to place the pressure valve at the end of the condenser coil, but here we have practically the same results, for, when the oil under pressure escaped from the valve, it came away surcharged with gas, like an aerated water when the cork is drawn, and that meant loss of material as well as risk from fire, and not only so, but, all your fittings being under pressure could not be kept tight enough — the expanding and contracting action which was always at work.

The method I propose to employ gets over all these difficulties, and that in a very simple way. I place my pressure valve on the direct outlet from the still, and when the desired pressure has been overcome, the gases immediately escape into a large iron box surrounded with cold water, which acts as a condenser, and the pressure is here dis-

tributed over such a large area that it is practically reduced to nil (i. e., to atmospheric pressure). What condenses here runs out by an outlet at the bottom of the relief tank (as I will hereafter call it), and escapes at once through the condenser to the receiving tank; and what does not here condense rises up and over by an outlet at the top of the relief tank, and goes direct to the condenser, where it meets the condensed oil from the relief tank, and is condensed and run to receiving tank in the usual way. You will thus see that I get quit of all pressure immediately the gases leave the still, and by interposing this relief tank I am able to keep a hold of all the gases till they are condensed into liquid products, and the fittings are relieved of all pressure and remain tight.

Before proceeding with the conservative method of distillation, I would like to say a few words in further reference to the molecular condition of mineral oils. I conducted a number of very interesting experiments (which I need not trouble you with here), which led me to the conclusion that the molecular condition of mineral oils took the form of aggregated molecules, whose affinity for each other was very great, and these I have called compound molecules. Of course, they are of ultra-microscopic magnitude. These compound molecules are of different sizes, and in proportion as these are large or small so is an oil heavy or light in specific gravity. The cohesive force, by virtue of which its compound molecules are held together, is not the same in all mineral oils of the same specific gravity. Some [fol. 787] oils are more readily broken down than others. To put it popularly, they appear to me to keep together just like members of families; the larger the families you have together you have the denser oil, and according as you have a number of smaller families mixed through with the larger ones so you have oils giving light and heavier products in distillation. If you have a number of large families of stout and strong constitutions together, you will have a body capable of resisting a great amount of external force; in other words, you will have an oil which will not be readily broken down. If you have a number of large families together, and constituting an equally heavy oil as the other referred to, but the families are of a comparatively weakly constitution, it will take a less force to break them down,

and here you will have an oil which is easily cracked up; the cohesive force has not been so great as in the other instance here referred to. In short, the compound molecules break down in proportion as this cohesive force is overcome; and, if you push this force to the extreme, I have no doubt you will at last rupture the chemical affinity, and your ultimate molecule will be broken up into its component parts, hydrogen and carbon, the former escaping as a permanent gas, and the latter being left behind in the still; the great heat or force employed unties the bond of chemical affinity and liberates the atoms. I have now come to the last heading of my paper, viz.—

The Conservative Distillation of Mineral Oils

—From what I have said before, you will readily understand that if we wish to obtain an oil of maximum density and viscosity, we must distil it at as low a temperature as possible, and as quickly as possible, so that the oil vapours be preserved from being broken down by being kept too long in the region of great heat. Even in the most approved system at present of distilling mineral oils, we have not got over the difficulty which meets us when distilling for lubricating oils of high density and viscosity.

I have long been under the impression that we obtain far too low a percentage of these high density oils from the crude material we start with, and I think I have taken a step in the right direction in bringing before you, for the first time, this new form of still. Before describing the apparatus in detail, I think a few words of explanation as to the advantages to be gained by this form of still over those [fol. 788] at present in use will not be out of place. In distilling mineral oils as at present, the contents of your still are gradually getting the denser as you proceed, and by the time you are three-fourths through with the distillation you have a very viscid material to deal with, and this; from its non-conducting properties and density, has a great tendency to cling to the bottom of the still and prevent the necessary heat passing to evaporate it quick enough, and hence you require to force more heat into the still to overcome the resisting action of the thick residue. In this way the sides of the still, above the level of the oil inside, get excessively heated, and the oil vapours coming in

contact with this radiant heat are very apt to get broken down to a considerable extent, and thus yield a degraded distillate. If you pump in fresh oil on the top of this heavy residue, I find this oil does not, to any great extent, dissolve the residue in the still, but lies on the top of it; and while this latter portion is being distilled, a granular pitch is being formed at the bottom of the still, and if you push your heat further you will convert this gradually into coke of a very hard nature, and you will have a considerable loss through the formation of permanent gas.

I have seen this very beautifully illustrated on taking off the end of the horizontal still I was working with. The layer of coke next the skin of the still was exceedingly dense in character, and it gradually got less dense as it increased in thickness, and towards the upper surface it was quite granular, and this again was topped with a pitch which remained plastic on cooling. You will thus see that practically all the heat which was distilling the oil on the surface was obtained from the upper sides of the still, and not from the bottom—very bad economy of heat indeed. This excessive heat at the end of the distillation is the main cause of the short life of many of our oil stills.

With regard to this new form of still which I have the honour to place before you (see Plate No. 4), I think I have surmounted these difficulties. You will observe that in vertical section it takes the form of a cross, +, the head of which forms the attachment of the Swan neck; the wings forming the distilling chamber, and the tail-piece being that portion by which the pitchy residues are kept separate from the lighter oil under distillation. By means of a ball-cock arrangement, the still is kept always at a uniform [fol. 789] depth. The heat is applied to the under surface of the wings all round the still, and as this distillation goes on, the heavy residue, which forms, gradually finds its way to the bottom of the tail-piece, and remains there away from the source of heat, and when sufficiently heavy can readily be removed by the cock arrangement found there for that purpose. In this way you should never be troubled with coke forming, and your still should always remain clean. The depth of oil, through which the distilling heat has to pass, is always a constant factor, and the nature of the oil under the action of this heat is pretty nearly uniform. The bottom of the main body of the still

or distilling chamber, as I call it, is inclined downwards and inwards, and this facilitates the withdrawal of the residual matter from this chamber, as it is formed, to the cooler region at the tail-end of the still. You thus avoid all forcing of fires; no part of your still gets unduly heated; your gases have a shorter travel; and you work practically with a uniformly steady heat, the energy of which is employed in doing useful work.

I am strongly convinced, from the experiments I have already made, that such a form of still as I have placed before you this evening, whether worked in conjunction with a vacuum pump or not, would produce from a given oil a larger percentage of heavier oils, of greater viscosity, and also of high melting-point paraffin, than any other still at present in use.

References to Plates

Plate No. 1:—Figures 1 and 2 are respectively a transverse vertical section and a longitudinal vertical section of the apparatus. The same reference letters mark the same parts when repeated, two or more similar parts are distinguished by numerals combined with letters. A, boiler-still; B1 to B4, compartments in still open at bottom; C, vertical partitions; D, furnace; E, flue; F, side ports; G, return flues at the sides of the boiler; H, horizontal flue communicating with return flues G at their front ends; J, additional ports communicating between E and G fitted with dampers; K, feed pipe; L1 to L3, gas inlets to condensers; M1 to M3, condensers; N, swan neck going to general condenser; P, cold water supply pipes going to condensers; Q, hot water outlets from condensers; R, water jacket attached to end compartment of still; S, cold water supply to water jacket with hot water outlet; T, pitch pipe from still to sampling vessel; U, pitch sampling vessel; [fol. 790] V, sampling cock; W, run-off pitch cock; X, stricture valve on swan neck regulating outflow of gases; Y, pyrometer.

Plate No. 2.—Radiant Heat.—Shows a longitudinal vertical section and a part of primary still. A, part of primary still; B, swan neck outlet; C, continuation of swan neck going to condensing worm; D, condensing worm in cold water tank; E, stop valve; F, branch pipe from swan neck to super-heater; G, stop valve; H, super-heater, which

may be filled with scrap-iron; J, firebrick casing to moderate and equalise heat on super-heater; K, extension of boiler flue space; L, damper to regulate heat on super-heater; M, connection between super-heater and condenser; N, stop valve; P, outlet from condenser in form of siphon, and which may be extended downwards into the oil sufficiently to hold a column corresponding to the degree of vacuum required; Q, general receiving tank; B, outlet for air or incondensible gas, also a connection for vacuum pump if required.

Plate No. 3.—Distilling under Pressure.—Shows a longitudinal vertical section and part of primary still. A, part of primary still; B, swan neck outlet; C, continuation of swan neck leading to condensing worm; D, condensing worm in cold water tank; E, stop valve; S, pressure valve; T, weighted lever of pressure valve; U, branch pipe from pressure valve to relief tank; V, relief tank in outer vessel of cold water and acting as condenser; W, cold water vessel holding relief tank; X, outlet for gases from V going to condenser; Y, outlet for condensed oil from V going through condenser to receiver; Z, inverted siphon leading off any oil condenser behind E to receiver.

[fol. 791] PETITIONER'S EXHIBIT No. 107

Petroleum, a Treatise on the Geographical Distribution and Geological Occurrence of Petroleum and Natural Gas; the Physical and Chemical Properties, Production, and Refining of Petroleum and Ozokerite; the Characters and Uses, Testing, Transport, and Storage of Petroleum Products; and the Legislative Enactments Relating Thereto; together with a Description of the Shale Oil and Allied Industries.

By Boverton Redwood, F.R.S.E., F.I.C., Assoc. Inst. C.E.,

Vice-President of the Society of Chemical Industry, Fellow of the Chemical, Geological, and Royal Geographical Societies, Member of the American Chemical Society, Honorary Corresponding Member of the Imperial Russian Technical Society (Baku Division), Consulting Adviser to the Corporation of London under the Petroleum Acts, Chemical Adviser to the Oil Trade Section of the London Chamber of Commerce, &c.,

Assisted by Geo. T. Holloway, Assoc. R. Coll. Sc., F.I.C., and Other Contributors

In Two Volumes, with Numerous Maps, Plates, and Illustrations in the Text

Vol. I

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(Pages 317 to 322)

sions. The heating may be effected by underfiring only, or by underfiring aided by lateral flues, or, as in the arrangement figured, by combining both the side heating and the [fol. 792] underfiring, with flues which pass through the still. The furnace gases travel along the lines, Z_1 Z_1, and after traversing the two side channels, pass through the flues, K, extending through the still, and thence to the chimney, along the line Z_2.

This form of still can be constructed to take a charge of from 400 to 700 barrels of oil at a time. It is provided with a safety stop-valve, E_1, and a gauge, S, fitted with a series of small taps at various heights, so that the level of oil in the still may be ascertained. When the oil surface sinks below the flues, K, the damper, T, is closed, and dampers, T^1 and T^2, are opened, the heat then no longer traversing the internal flues, but passing direct to the chimney.

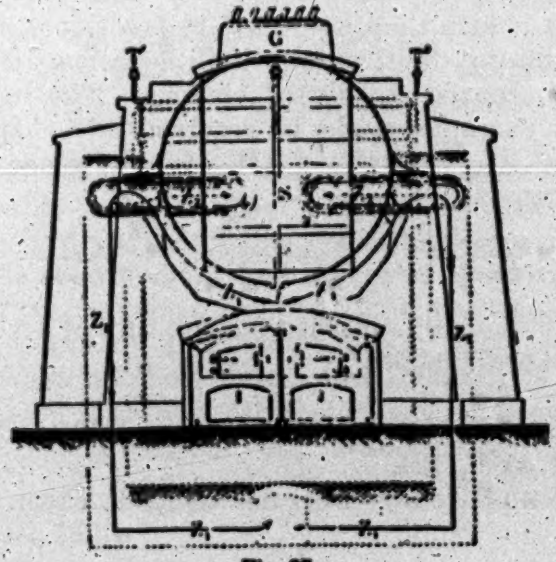

Fig. 97.

These stills are set in batteries with a common wall and a common chimney. They are usually heated by petroleum residues, and sometimes the distillation is conducted with the aid of superheated steam. The dome, G, usually has from five to seven pipes leading to the condenser, which is common to several stills. The stills are usually set in the open air, and the upper part is often not walled in, only tile coverings or a metal casing with a packing of glass wool or slag being used.

The "cracking process," whereby a considerable quantity of the oil which is intermediate betwen kerosene and lubricating oil is converted into hydrocarbons of lower den- [fol. 793] sity and boiling point, suitable for illuminating purposes, is one of great scientific and technical interest.

It is generally understood that the products of fractional distillation, even in the laboratory, are not identical with the hydrocarbons present in the crude oil, but are in part produced by the action of heat upon them. This was plainly stated by Professor Silliman in the earliest stages of development of the American petroleum industry. An important paper bearing on the subject was published in 1871 by Thorpe and Young[1], as a preliminary note on their experiments on the action of heat under pressure on solid paraffins. They found that the paraffin was thus converted, with the evolution of but little gas, into hydrocarbons which were liquid at ordinary temperatures. In an experiment on 3,500 grammes of paraffin produced from shale (melting point 44.5° C.), they obtained nearly 4 litres of liquid hydrocarbons, which they subjected to fractional distillation, and on exam-ing the fraction distilling below 100° C., they found it to consist mainly of olefines. The hydrocarbon $C_{20}H_{42}$, for example, might be resolved into $C_5H_{12}+C_{15}H_{30}$, or $C_6H_{14}+C_{14}H_{28}$, or $C_7H_{16}+C_{13}H_{26}$, &c., the general equation of the decomposition being—

$$\underset{\text{Paraffin.}}{C_nH_{n+2}} = \underset{\text{Paraffin.}}{C_{n-p}H_{2(n-p)+2}} + \underset{\text{Olefine.}}{C_pH_{2p}}$$

The product actually obtained is a mixture of several paraffins and several olefines.[2]

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[1] Proc. Roy. Soc., March 9, 1871, xix., 370; and Chemical News, 1871, xxiii., 124.

[2] Thorpe and Young, Ber. der deutsch. chem. Gesellsch, 1872, 536.

Experiments based on these results, which were carried out at Riebeck's Montan Works in Saxony, showed that the light oils obtained from the heavy distillates of lignite tar, and from Baku petroleum residues, were practically identical.

The cracking process practically consists in distilling the oils at a temperature higher than the normal boiling points of the constituents which it is desired to decompose. This may be brought about by distillation under pressure, or by allowing the condenser distillate to fall into the highly treated residue in the still. The result of this treatment is that the comparatively heavy oils undergo dissociation, as in the experiments of Thorpe and Young, into specially lighter hydrocarbons of lower boiling points, and the yield [fol. 794] of kerosene from ordinary crude petroleum may thus be greatly increased.

In his work on Petroleum Distillation (New York, 1884), Leet describes the cracking process as having been accidentally discovered in the winter of 1861. The man in charge of a 16-barrel still at Newark, New Jersey, built a "strong fire" under the still after about half its contents had been distilled off, and left with the intention of returning in half an hour. It was not, however, until after four hours that he returned to the refinery, and he then found that a light coloured distillate, of lower density than that which was being obtained when he left, was issuing from the condenser. As the result of experiments to which this discovery led, it was found that a portion of the distillate had condensed upon the cooler upper part of the still, and had dropped back into the still, where the temperature was sufficient to cause its dissociation into products of lower boiling point.

These and other similar observations soon led to the setting of stills with the upper parts wholly uncovered, so that the desired partial condensation shall occur, and the less valuable intermediate hydrocarbons be converted into kerosene in the manner described. The exact action of the cracking process on petroleum is not fully understood. Veith[1] considers it to be a dissociation followed by polymerisation, and says that the cracked oils have not been properly examined. The process is very largely employed, but the

[1] Das Erdöl, 1892.

product is not identical with, and probably not equal in quality to, the natural distillate. It is asserted that such oil is inferior in light-giving power, and more readily acquires a dark colour on keeping. It is certain that the smell of the cracked oil is stronger, and that in the chemical treatment, a much larger quantity of sulphuric acid is required. The cracking does not commence until after the more volatile products, including the distillate from which high-test oils having a fire-test of from 120° to 150° F. are made, have been obtained. The fires are then damped, and the distillation continued slowly, to permit of the necessary condensation. During the cracking, a considerable quantity of permanent gas is evolved, and this is usually burned beneath the still.

[fol. 795]

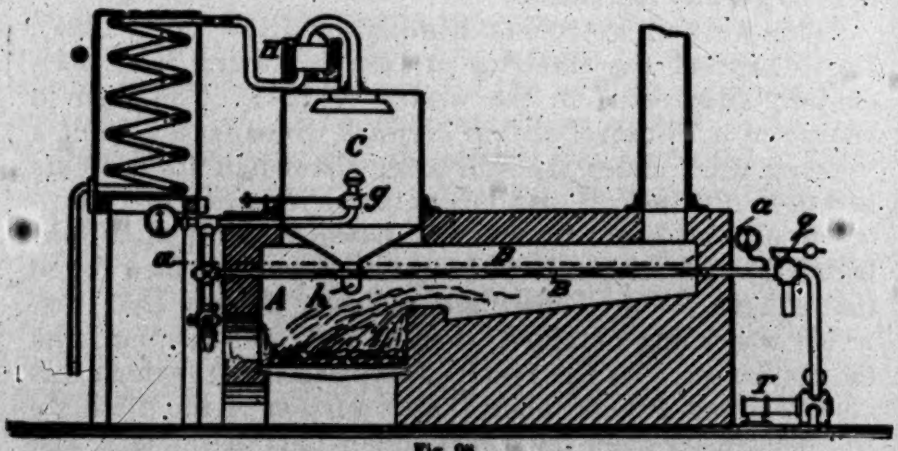


Fig. 9a.

A large number of arrangements for carrying out the cracking process have been proposed and patented, probably the earliest, directly bearing on the subject, being that of James Young, who in 1865, patented (No. 3,345) his "Improvements in treating hydrocarbon oils." In this patent, the distillation is described as being conducted in a vessel having a loaded valve or a partially closed stop-cock, through which the confined vapour escapes under any desired pressure. Under such conditions, distillation takes place at higher temperatures than the normal boiling points of the constituent hydrocarbons of the oil, and a partial cracking results. The patent was taken out for the treatment of shale oil, a pressure of about 20 lbs. to the inch being recommended.

In 1887, a patent was granted in this country to Benton, of Titusville, Pa.,[1] for "improvements in the methods and means of refining crude and refuse petroleum and the like." The process consisted in pumping "the refuse of petroleum oil, tar oils, and other heavy mineral oils," under a pressure of 285 lbs. or more to the square inch, through a series of pipes heated in a furnace, and allowing the products to escape into a vapour chamber. The apparatus, which was said to produce lighter hydrocarbons from the products specified, is illustrated in Figs. 98 and 99. It consists of a series of pipes, B, heated by means of a furnace, A, and communicating on one side with a force-pump, T, and on the other with a vapour chamber, C, which may be heated or partially exhausted. The pressure is regulated by a stop-valve, *g*, a weighted check-valve, *q*, being also provided. The un-volatilised liquid passes from the chamber, C, at *h*, and the vapour traverses a condenser, H.

[fol. 796]

Fig. 99.

The process patented by Dewar and Redwood in 1889,[2] consists in the use of a suitable still and condenser in free communication with each other—i. e., without any valve between them—the space in the still and condenser not occupied by liquid being charged with air, or carbonic acid gas, or other gas, under the required pressure, and the condenser being provided with a regulated outlet for condensed liquid. An objectionable feature of the system of allowing the vapour to escape from the still to the condenser through a loaded valve—viz., the irregularity of the distillation—is thus removed, and the benefits of regular

[1] Haddan's patent, No. 1,922.
[2] No. 10,277.

vaporisation and condensation under high pressure are obtained. The ordinary process of cracking, which consists in allowing the less volatile portions of the vapour to become condensed in the stillhead, and fall back into the liquid below, is both slow and comparatively ineffective, besides involving considerable waste of heat, but if desired, the head of the still or retort employed in the Dewar-Redwood process may be so constructed as to produce partial condensation. The apparatus for carrying out the process may be arranged in various ways, one form being shown in Fig. 100. The lower portion of the figure is a sectional plan on the line X X. A is a fire-place, with fire-door, A^1, and ashpit door, A^2, suited for regulating admission of air as required. Instead of a fireplace with grate for burning solid fuel, a burner for liquid or gaseous fuel may be employed. Above the combustion chamber, B, is placed a metal retort, C, which is enclosed within a refractory casing, C^1, to protect the metal from excessive local heating. The encased retort is situated in a heating chamber, B^1,

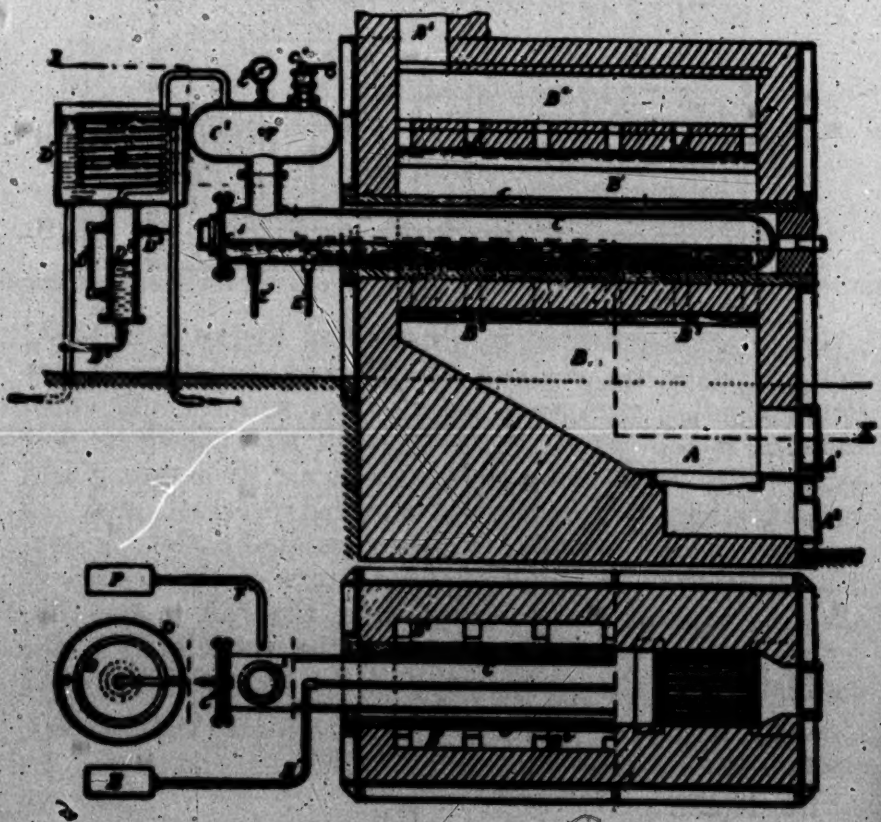


Fig. 100.

[fol. 797] into which the hot products of combustion ascend by side ports, B^2, and from which they pass by central ports, B^3, into a flue, B^4, communicating with a chimney, B^5. The front part of the retort, C, communicates freely with a stillhead, C^2, provided with a pressure-gauge, C^3, and safety-valve, C^4. The exposed end of the retort, C, is closed by a readily removable cover, C^5, provided with a glass gauge to show the level of the liquid in the retort. D is a pipe-coil situated in a tank, D^1, in which circulation of water is maintained. The upper end of the coil, D, communicates by a pipe with the stillhead, C^2, and its lower end opens into a hollow column, D^2, which is provided with a glass gauge, D^3, and has at the bottom an outlet pipe, D^4, furnished with a stopcock or valve. E is a pump for forcing the oil to be treated, by a pipe, E^1, into the retort, C, this pipe preferably extending nearly to the further end of the retort. By another pipe, E^2, furnished with a cock or valve, the contents of the retort can be drawn off, or this pipe may com-[fol. 798] municate with a second retort, which in like manner may be connected with a third, so as to form a series of any required number. F is an air-compressing pump, by which air or suitable gas is forced by a pipe, F^1, into the stillhead, C^2, or it might be into any other part of the apparatus which is in communication with the stillhead. The retort, C, being partly charged with oil by the pump, E; and the spaces in the retort, C, in the stillhead, C^2, and in the condensing coil, D, and the column, D^2, being charged with air or gas at the desired pressure: the retort is heated, vaporising the oil under pressure. The oil vapour is condensed in passing through the coil, D, and the liquid distillate collects in the column, D^2, and is drawn off, either continuously or intermittently, into suitable receptacles, in which such gas as may be dissolved in the liquid is liberated and can be collected. By a pipe and cock, or a suitably loaded safety-valve, D^5, gas may be withdrawn from the space above the liquid in the column, D^2. Although only one retort and condenser are shown, there may be several sets of these in communication with the oil and gas pumps, or with each other, suitable cocks or valves being provided in the communicating pipes, so that the several retorts may be worked simultaneously, or in rotation. From time to time, the cover, C^5, of the retort may be removed to clear

out residue. During the distillation, such of the vapour as may be condensed in the stillhead, C^3, or such liquid as may prime up into the stillhead, flows back into the body of liquid in the retort. By regulating the heat and pressure to which the retort is subjected, the character of the distillate may be varied. The proportions of the several parts of the apparatus may be altered, and if necessary, means of cooling may be applied to the stillhead, C^3. With such an apparatus, intermediate and heavy oils may be readily converted to a considerable extent into lighter oils suitable for use in ordinary mineral-oil lamps, and even mineral spirit of low boiling point, capable of being employed for the carburetting of coal gas, may be produced.

Fig. 101 shows a cast-iron still used in Russia in carrying out the cracking process. It is in the form of a cast-iron cylinder with a hemispherical bottom, having an outlet, S, provided with a tap, through which the residue may be drawn off. In some cases, distillation is carried to dryness, the coke being then removed through a manhole, D. When superheated steam is employed in the distillation, as is [fol. 799] often the case, the coke is of a somewhat soft nature, and does not adhere firmly to the still. The flame from the furnace, passes over a bridge, through a perforated block, N_1, through a flue, Z_1, round the lower part of the still and through a flue, Z_2, round the upper part. By means of dampers, the heat may be diverted from the flue, Z_2. The crude oil, or residue from a previous distillation,

[fol. 800] PETITIONER'S EXHIBIT 108

United States Patent Office

William Spears, of Jamestown, New York

Letters Patent No. 107,734, dated September 27, 1870

Improvement in the Manufacture of Hydrocarbon Oils

The Schedule Referred to in These Letters Patent and Making Part of the Same

To all whom it may concern:

Be it known that I, William Spears, of Jamestown, in the county of Chautauqua and State of New York, have

invented a new and useful Improvement in the Manufacture of Hydrocarbon Oil; and I do hereby declare that the following is a full, clear, and exact description thereof, which will enable others skilled in the art to make and use the same.

The object of this invention is to produce a highly valuable hydrocarbon oil or liquid, for illuminating or other purposes, from the products of distillation in the process of manufacturing oils from crude petroleum, and consists in uniting (by the application of heat) the first and most volatile product of distillation (benzine) with the refuse tar, thereby forming a compound from which a highly valuable oil is distilled.

In carrying out my invention and discovery, I place the benzine and the tar (in suitable proportions) in a tank or vat of proper capacity, and raise the temperature of the mixture sufficiently high to cause the two substances to perfectly unite.

The temperature may be raised by means of steam, or by heat applied in any other manner.

By the application of heat the dirt and clay, or other foreign matter contained in the tar, is precipitated, and the compound may be distilled most successfully, the yield of oil being much greater than from common crude petroleum.

The specimen marked C is the benzine and tar combined according to my invention.

D is the oil distilled therefrom.

Having thus described my invention,

I claim as new and desire to secure by Letters Patent—

An illuminating oil, manufactured by distilling a chemical combination formed of benzine and tar, in the manner specified.

William Spears.

Witnesses: Jesse M. Healy, James M. Yoony.

[fol. 801] PETITIONER'S EXHIBIT 109

United States Patent Office

John F. Boynton, of Syracuse, New York

Improvement in Liquids for Carbureting and Enriching Gases Used for Illuminating and Heating

Specification Forming Part of Letters Patent No. 58,054, Dated September 18, 1866

To all whom it may concern:

Be it known that I, John F. Boynton, of the city of Syracuse, in the county of Onondaga and State of New York, have made a new and useful Improvement in Liquids for Carbureting and Enriching Gases used for Illumination, and in their application for the purpose of carbureting gases and air; and I hereby declare the following to be a full and exact description of the same.

The value of gases for illumination, when burned in the ordinary manner, depends upon the relative proportion of carbon and hydrogen. If hydrogen gas is in excess, combustion will produce a large amount of heat and but little light. If carbon is in excess, it is difficult to keep the flame from smoking.

There are certain kinds of coal which, when distilled in the manner usual in gas-works, produce gas rich in light-giving properties; but it is not always practicable to obtain such coal, and gas from good coal is liable to deteriorate when conveyed in pipes long distances, or when it remains for some time in contact with cold water. Hence it has long been an object to find some practical mode of enriching poor gases, and for restoring that which has become poor by the condensation of the light oily hydrocarbons, upon which its illuminating property is known to depend.

The first mode proposed for accomplishing this was to saturate the gas at or near the meter with the vapors of one or more of the products obtained by the distillation of gas-tar, or tar from gas-works. These products are very numerous, but all contain a large proportion of carbon. The lightest of these has long been familiar to the public

under the name of "benzole" or "benzine." This, at ordinary temperatures, is a light volatile liquid of a specific gravity of about 0.85. The benzole of commerce is generally a mixture of the benzole of the chemist with homologous hydrocarbons, all derived from coal in the usual process of manufacturing illuminating-gas, and is more properly designated "naphtha," or "rectified naphtha."

The least volatile of these hydrocarbons is naphthaline, which, when separated from the others, is solid at the ordinary temperature of the air. For the sake of classification, all these hydrocarbons are designated the naphthaline series of hydrocarbons.

The formula which expresses the composition of benzole is C^{12} H^{6}, and naphthaline, C^{20} H^{8}. The other members of the series have a composition intermediate between these two. Being all rich in carbon, their addition to gas will greatly increase its illuminating power. But after a long series of practical experiments the use of these liquids failed of general introduction, principally for the reason that these liquids are so easily affected by changes of temperature that the gas carbureted by them is not uniform, the degrees of carbureting being excessive in warm weather and failing almost entirely in cold weather. The same difficulty attends the carbureting of air to produce what is known as air-light or benzole-light, and in carbureting the mixed gas produced by what is known as the "water-gas process."

The development and general introduction of petroleum a few years ago brought before the public another class of hydrocarbons, resembling in many respects the volatile liquids from gas-tar, but of very different chemical constitution, and also different as respects their freezing-point.

From some resemblance to the liquids from the tar of gas-works, the light products from petroleum of a specific gravity of .70 to .75 are frequently called "benzole" or "benzine," and under that term, or as "gasoline," "naphtha," "carbon spirits," and other commercial names, have gone into use in the arts, and have been largely employed within the last few years, especially for carbureting air and gas. That one which corresponds most nearly in its general appearance to the benzole of gas-tar has the chemical

formula C^{12} H^{14}. Other members of the group have been separated from petroleum, some more and some less volatile, but all having an excess of hydrogen, while in the gas-tar products the carbon is in excess.

These liquids do not congeal at the lowest temperature met with in our latitudes, and on that account present a great advantage as carbureting-liquids. But as carbureting-liquids these are defective, for the reason that the [fol. 802] amount of carbon they contain is much smaller than in the gas-tar liquids. For carbureting gas they are also defective, for the reason that the vapors of the petroleum liquids do not readily combine with coal-gas.

After numerous experiments in carbureting gas and air with both of the above-mentioned classes of hydrocarbons, the idea occurred to me to combine them. The result was such as I expected, as these two series of liquids readily combine, being mutually solvents one of the other.

The nature, therefore, of my invention consists in making liquids for carbureting and enriching coal-gas, air, water-gas, and the like by combining hydrocarbons of the coal-tar or naphthaline series with hydrocarbons of the petroleum series, or their equivalents.

By this process I produce liquids suitable for carbureting either air or gas, which may be depended upon at all seasons of the year; and by the application of my invention the gas from cheap coal may, at small expense, be made equal in illuminating power to gas from the richest and most expensive coal.

Where coal-gas cannot be obtained, my compound liquids may be applied to the carbureting of air or water-gas, so as to produce a good and cheap light.

The compound liquids produced by my invention do not congeal, since the petroleum spirits act upon the hydrocarbons of the naphthaline series as alcohol does upon water. They are sufficiently rich in carbon to render the poorest coal-gas suitable for illumination. Besides, by using the very light spirits from petroleum, I can use some of the heavy oils from coal-tar, which would otherwise not be sufficiently volatile. The light and heavy vapors of the different series of hydrocarbons have so strong an affinity for each other that the light vapor will carry with it the heavy,

as water is carried over by the vapor of alcohol in distillation.

I have mentioned especially the hydrocarbons from petroleum, for the reason that they are most abundant; but the liquid oils derived by distilling coals at a low temperature are substantially the same in constitution as these products of petroleum. The so-called "paraffine-oils" belong to this class, and may be considered as the equivalent of the oils from petroleum.

To enable otherse skilled in the art to make and use my invention, I proceed to describe one method of preparing the fluid.

Of petroleum products rectified, I mix with the products of gas-tar in the following proportions, viz: Three parts of Naphtha from gas-tar, three parts of benzole from gas-tar, two parts of petroleum spirits or gasoline. These may be used after being simply but thoroughly mixed; but it would be better to redistill them together before using, stopping distillation at about 350° Fahrenheit. Or I take the unrectified products in quantities sufficient to insure the above proportions, mix them together, and distill over till the gravity is the same as that of the mixture of rectified products above given.

If the gas to be carbureted is very poor in illuminating properties, I add to the above-named proportions one gallon of petroleum spirits of specific gravity of about .70 and one gallon of gas-tar benzole.

I have indicated above the proportions I prefer; but these may be greatly varied, and must, to some extent, depend upon the quality of the gas to be enriched, and also upon the gravity of the liquid used.

The liquids produced by the above process may be applied by means of my multipliers, or by any of the machines in use for similar purposes that may be properly constructed.

Having thus described my invention, what I claim, and desire to secure by Letters Patent of the United States, is—

1. The improved liquids for carbureting or enriching gas or air produced by combining one or more hydrocarbons derived from petroleum or its equivalent with one or more hydrocarbons of the coal-tar series.

2. Carbureting or enriching coal-gas, water-gas, or air by combining with them the vapor of a liquid made by combining hydrocarbons of the coal-tar series with those of the petroleum series, substantially as herein described.

3. The method or process herein described of manufacturing liquids for carbureting or enriching gas or air by combining one or more hydrocarbons derived from petroleum or its equivalent with one or more hydrocarbons of the coal-tar series.

John F. Boynton.

Witnesses: J. J. Coombs, Jno. C. Winn.

[fol. 803] PETITIONER'S EXHIBIT 110

United States Patent Office

John A. Bassett, of Salem, Massachusetts

Letters Patent No. 65,866, dated June 18, 1867

Improved Hydrocarbon Fluid for Carburetting Gas

The Schedule Referred to in These Letters Patent and Making Part of the Same

To all whom it may concern:

Be it known that I, John A. Bassett, of Salem, in the county of Essex, and State of Massachusetts, have invented a new and useful Hydrocarbon Fluid for Carburetting Gases; and I do hereby declare that the following is a full and exact description of the same.

The nature of my invention consists in producing hydrocarbon liquids used for the carburation of gases for illuminating purposes, by combining the volatile portions of the results of the petroleum and coal distillation, the object being to provide a fluid for carburetting purposes which shall have the proper proportions of carbon and hydrogen, shall be readily affected by changes of temperature, and not liable to condensation in cold weather; and it consists for this purpose of a combination of the

light products of the distillation of petroleum with the light products of the distillation of coal. The petroleum products should have a gravity of about 79° B. A higher gravity may be used, if desired. The coal products should be rectified, and should be from 28° to 30°.

I mix these two products in the proportion of one part of the light products of coal to five parts of the light products of petroleum. Different proportions of the coal and petroleum products may be used, varying the mixture according to the temperature or the result desired. The coal products all contain an excess of carbon. The petroleum products all contain an excess of hydrogen. The coal products do not vaporize regularly, and are liable to become solids at low temperatures, while the excess of carbon they contain renders their use desirable for carburetting purposes. The petroleum products vaporize uniformly, do not congeal at low temperatures, and perfectly dissolve and mix with the coal products. The mixture, therefore, of these hydrocarbons produces the best photometric results, and makes practicable the conditions for carburetting gases at varying degrees of temperature.

Having thus fully described my invention, what I desire a patent for, is——

1. A hydrocarbon liquid used for the purpose above named, produced by the combination of the coal and petroleum carbons, as described and set forth.

2. Adding to the photometric value of gases by carburetting with the hydrocarbons produced by the combination of the light products of the distillation of coal and petroleum.

3. The process, substantially as set forth, of manufacturing hydrocarbons for carburetting gases by combining the hydrocarbons of coal and petroleum in variable proportions, as set forth.

J. A. Bassett.

Witnesses: Chas. A. Stoddard, W. D. Chesebrough.

[fol. 804] PETITIONER'S EXHIBIT 111

United States Patent Office

Henry V. Walker, of Brooklyn, New York, Assignor to the Maas & Waldstein Company, of Newark, New Jersey, a Corporation of New Jersey

Solvent for Pyroxylin, &c., and Process for Making the Same

972,953. No Drawing. Specification of Letters Patent. Patented Oct. 18, 1910

Application Filed January 21, 1909. Serial No. 473,499

To all whom it may concern:

Be it known that I, Henry V. Walker, a citizen of the United States, and resident of Brooklyn, in the county of Kings and State of New York, have invented certain new and useful Improvements in Solvents for Pyroxylin, &c., and Processes for Making Same, of which the following is a specification.

The preferred method of practicing my present process and of obtaining the novel solvents of my present invention is related to my process for making hypochlorous acid, the subject of my application, simultaneous herewith, for United States Letters Patent Serial No. 473,498, and is also related to my process for making chlorhydrins, the subject of my application, simultaneous herewith, for United States Letters Patent Serial No. 473,497.

As examples of the new solvents within my present invention, I have specifically named gas naphtha olefin oxids, and will now proceed to describe their method of preparation and the characteristics of the solvents themselves.

My preferred starting material is so-called gas-naphtha, a by-product of the ordinary commercial treatment of petroleum. Thus, in the process of refining crude petroleum, the oil is subjected to distillation, the lighter products, such as naphtha and benzin, coming over first. These are followed by the burning oil fraction. At a certain stage of this period of the distillation, it is found that the product coming over is of much lower boiling point, gravity and

flashing point than that preceding it. This peculiarity is attributed to a cracking up of the higher hydrocarbons under the influence of the high temperature prevailing in the distillation. It is usual to run the distillation until the product has again risen in gravity, etc., to that of the initial burning oil fraction. This secondary product which is collected separately is then redistilled, yielding a distillate called "gas-naphtha" and a residue which is added to the burning oil fraction. This material known in the refineries as gas-naphtha has been so called from the use to which it has heretofore been put, namely, the manufacture of gas for heating purposes and the enrichment of illuminating gas. Whereas American petroleum consists almost exclusively of saturated hydrocarbons or paraffins, the gas-naphtha contains about 40% of olefins and about 60% only of paraffins. Its boiling point ranges from 35° to 125° centigrade. It is believed that its olefins range from 5 to 8 carbons and that they are primary in structure. For example, the C_6 olefin may be represented by the formula:

$$CH_3—CH_2—CH_2—CH_2—CH=CH_2.$$

As part of the process, I convert the olefins of this gas naphtha into chlorhydrins. It might be thought that such a mixture of olefins and paraffins as is contained in this gas-naphtha would react with hypochlorous acid produced in any of the usual ways to form chlorhydrins (although so far as known to me no chlorhydrin or oxid of a primary olefin having five or more carbons has been so produced) but it was found not to be so. There are two described methods of preparing hypochlorous acid. The first of these depends essentially upon the reaction of chlorin with mercuric oxid. This method is too expensive to be thought of on account of the great cost of the mercuric oxid employed. The second of these comprises the treatment of hypochlorites of sodium, or calcium, with a dilute acid. In each case free chlorin was present, the yield of hypochlorous acid was small and its solution was dilute. Both of these methods, therefore, were unavailable. I was, therefore, obliged to find another method of producing the hypochlorous acid. I discovered that if there was added to a solution of a suitable hypochlorite, for instance, hypochlorite of soda, a sufficient quantity of a suitable bicarbonate, for instance, bicarbonate of soda, to convert both the

free alkali and the sodium in combination in the hypochlorite, into sodium carbonate, then a solution was obtained which contained hypochlorous acid, free from chlorin and which reacted readily with the olefins of the gas-naphtha.

I utilize this new process of making hypochlorous acid to [fol. 805] make the aforesaid chlorhydrins from the gas-naphtha olefins as follows: Thus, the gas-naphtha, comprising a mixture of olefins and paraffins as stated or other suitable material containing the olefins, is first placed in a vessel provided with means for agitating and cooling its contents. In another suitable vessel is placed a solution in water of a suitable hypochlorite, for instance, hypochlorite of soda, dissolved in water. It is preferable to use a separate vessel as stated, but not at all essential, since the gas-naphtha, hypochlorite and bicarbonate of soda or the equivalent materials may be all three mixed together and allowed to react in the same vessel. A solution of the hypochlorite containing from 15 to 25 per cent of NaOCl is of convenient strength. To this is added a sufficient quantity of a soluble bicarbonate of a fixed alkali, preferably bicarbonate of soda, to react therewith to form hypochlorous acid. A proper proportion to employ is about 75 parts of the hypochlorite of soda (NaOCl) to about 85 parts of the bicarbonate of soda ($NaHCO_3$). The bicarbonate may be added in the form of a saturated aqueous solution, or mixed with an amount of water insufficient for solution or in the dry state. There is no free chlorin produced. The mixture of hypochlorite and bicarbonate of soda in which the hypochlorous acid formed is then added to the vessel containing the gas naphtha, or other material, and the contents are agitated and cooled. The reaction will take place at ordinary temperatures without cooling, but the best results are obtained by preventing the rise of temperature due to the reaction and maintaining the temperature at or below 15° centigrade. This reaction should continue for about four hours. At the end of that time the oily portion of the liquid containing the chlorhydrins is allowed to separate from the aqueous portion of the liquid, the latter being drawn off and rejected. The oily portion is then washed with a small amount of water to remove any hypochlorite which might remain and it is dehydrated. If it is desired to accomplish such dehydration quickly, cal-

cium chlorid may be employed. If time is not essential, the water may be allowed to separate out by gravity. The discovery upon which this part of the process depends is that the chlorhydrins remain in the oily part of the liquid and not in its aqueous part. The paraffins, or residual hydrocarbons, which are mixed with the chlorhydrins are then removed. This is accomplished by distillation at a suitable temperature below the boiling point of the chlorhydrins, which is about 170° centigrade. Such a temperature is about 140° centigrade. Of course, the temperature during this step of the process must be lower than that at which the chlorhydrins will be carried over. After such distillation, the residual liquid consists of the chlorhydrins sought to be obtained.

The reactions apparently involved may be illustrated in connection with the C_6 olefin:

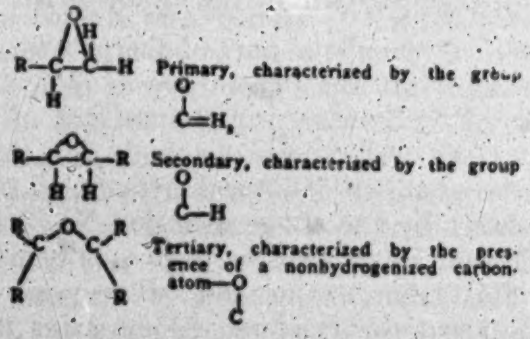
(1) $NaOCl+NaHCO_3=Na_2CO_3+HOCl$

(2) $C_6H_{12}+HOCl=C_6H_{12}.OH.Cl$
(Chlorhydrin of the C_6 olefin.)

In carrying out the above part of the process, it is advisable first to ascertain the percentage of olefins in the material employed by determining the amount of bromin absorbed, using the well known methods for this purpose. From this, the quantity of hypochlorous acid necessary to be used is shown by the above equation No. 2, a slight excess of such acid being used to insure as complete a conversion of the olefins as possible. The next step in the process is to treat the residual chlorhydrins produced as above with a suitable caustic alakli. For this purpose, I use the caustic alkalies, slaked lime, caustic potash or soda, preferring lime. In practice, to 1,000 grams of the chlorhydrins, I add a mixture of about 350 grams of lime mixed with about 1 liter of water. This chlorhydrin-lime mixture is heated to boiling in a suitable vessel with a return condenser for about one hour; it is then distilled with steam until no more oil passes over. This oil is separated from the water and agitated while cold with a 50% solution of caustic soda for the purpose of removing a small portion of impurities which may be present. It is then separated and is dehydrated with carbonate potash or calcium chlorid and distilled when it passes over as a water-white fluid.

The described distillate is a mixture of olefin oxids. If desired, it may be separated by fractional distillation into separate parts but this is a mere matter of expediency depending upon the particular use in view. These olefin oxids either separately or as a mixture constitute a novel solvent for pyroxylin and other substances.

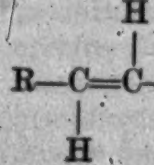
The gas naphtha, which is my preferred material for the production of the chlorhydrins, is a mixture of olefins and paraffins ranging from C_5H_{10} and C_5H_{12} to C_8H_{16} and C_8H_{18}. Its boiling point ranges from 30° C. to 125° C. By conversion into chlodydrins and decomposition with caustic alkali the olefins therein are converted into olefin oxids, from $C_5H_{10}O$ to $C_8H_{16}O$. The olefin oxids of five or more carbon atoms; heretofore produced have been of secondary or tertiary structure, whereas the olefins contained in the gas naphtha are of normal or primary structure. The oxids derived therefrom are therefore new bodies. [fol. 806] These differences in structure may be illustrated as follows, R representing any alkyl radical:



The facts upon which it is claimed that the new olefin oxids made from gas-naphtha have the primary structure are as follows:

1. The paraffins of American petroleum are of primary structure.

2. The olefins produced by the action of heat on the paraffins are also of primary structure,



(Armstrong and Miller, *Chem. Soc.* 1886 1, 79-93. *Ber.* (Ref.) 19,244.)

3. The olefin oxids prepared by me do not combine with water. This is a characteristic property of primary olefin oxids as distinguished from the secondary or tertiary oxids, which do combine with water to form glycols.

I am aware that Wurtz (A. ch. (4) 4, 184) has described the preparation of a hexylenoxid, an olefin oxid at one time thought to possess the primary structure, and which was prepared from the hexylen derived from mannite, but subsequent investigations have shown its structure to be secondary. (Henry *Compt. Rend.* 97,260.) The olefin oxids produced by me, therefore, are the first of the primary structure which have been made.

In some instances instead of separating the chlorhydrins from the paraffins as described, I may proceed as follows: After reacting on the gas naphtha with the hypochlorous acid mixture and separating the oily from the aqueous portion, I may distil the entire oily layer directly with caustic alkali, without separating the paraffins. The oily portion of the resulting distillate, after separation and dehydration in the usual manner, constitutes a noval solvent for various varnish gums, and when the percentage of olefins in the primary material is sufficiently high, for pyroxylin.

The mixture of olefin oxids produced as above described, and which constitutes a novel solvent for pyroxylin possesses several important advantages. By its use pyroxylin may be obtained in strong transparent films, properties heretofore commercially obtainable only by the use of amyl acetate as a solvent. My novel solvent is produced from petroleum, a domestic product available in unlimited quantities, as contrasted with amyl acetate, produced from fusel oil, mainly an imported product, of which the supply is necessarily limited. By the use of my novel solvent, pyroxylin may be employed for many indicated purposes for which it hitherto could not be used, because of the high cost of amyl acetate. My novel solvent may also be employed not only as a solvent for pyroxylin, but for other substances such as rubber, asphalt, sundry varnish gums such as copal, kauri and the like, and oils such as boiled linseed-oil. The new solvent may also be diluted with a number of other liquids such as benzin and similar petroleum products which while not themselves solvents for the materials dissolved by the new solvent,

nevertheless are miscible to a considerable extent with said solvent without annulling its solvent properties. For instance, if the new solvent is employed for dissolving pyroxylin it may be diluted with benzin even up to 30% in which dilution it will still dissolve pyroxylin although benzin itself does not dissolve this substance.

The olefin oxids derived from "gas naphtha" have a slight ethereal odor, are insoluble in water, and range in specific gravity from about 0.830 to about 0.855 and in boiling points from about 70° to about 145° C. according to their carbon content. They are colorless and readily miscible with the usual organic solvents, ether, alcohol, acetone, benzin, benzol, carbon tetrachlorid, and combine with hydrochloric acid with formation of the corresponding chlorhydrins.

What I claim as new and desire to secure by Letters Patent is:

1. The process of preparing a novel solvent which consists in mixing a bi-carbonate of a fixed alkali and a solution containing a hypochlorite of a fixed alkali, causing the mixture to react with gas naphtha, separating the oily from the aqueous portion of the reaction product, and distilling the oily portion with a caustic alkali.

2. The process of preparing a novel solvent which consists in mixing a bi-carbonate of a fixed alkali and a solution containing a hypochlorite of a fixed alkali, causing the mixture to react with gas naphtha, separating the oily from the aqueous portion of the reaction product, and distilling the oily portion with slaked lime.

3. As a new product of manufacture, an oxid of a primary olefin having approximately from five to eight carbon atoms, both inclusive.

4. As a new product of manufacture, an oxid of a primary olefin obtained from gas naphtha, having approxi- [fol. 807] mately from five to eight carbon atoms, both inclusive.

5. As a new product of manufacture, a mixture of a primary olefin oxid having approximately from five to eight carbon atoms, both inclusive, and a diluent, such as benzin, which mixture is capable of dissolving pyroxylin.

6. As a new product of manufacture, a mixture of an oxid of a primary olefin obtained from gas naphtha, and having approximately from five to eight carbon atoms, both inclusive and a diluent.

7. As new products of manufacture, the olefin oxids, derived from gas naphtha having a slight ethereal odor, insoluble in water, ranging in specific gravity from about 0.830 to about 0.855, and in boiling points from about 70° C. to about 145° C. according to their carbon content, being colorless and readily miscible with the usual organic solvents, ether, alcohol, acetone, benzin, benzol, carbon tetrachlorid, and having as a distinguishing chemical property that of combining with hydrochloric acid, with formation of the corresponding chlorhydrins.

Witness my hand this 19th day of January, 1909, at New York, N. Y.

HENRY V. WALKER.

Witnesses:
William R. Baird,
Stephen S. Newton.

[fol. 808] PETITIONER'S EXHIBIT No. 112

The Chemical News and Journal of Physical Science, with Which Is Incorporated the "Chemical Gazette," a Journal of Practical Chemistry in All Its Applications to Pharmacy, Arts and Manufactures

Edited by William Crookes, F.R.S., &c.

Volume 36, July-Dec., 1877

London: Published at the Office, Boy Court, Ludgate Hill, E. C., and Sold by all Booksellers

MDCCCLXXVII

(Page 140)

Conversion of the Normal Paraffins Into the Benzole Series

To the Editor of the Chemical News.

SIR: May I have a space as of old in your hospitable pages for a discovery which I think is of considerable interest both to scientific and industrial chemistry—conversion of the normal paraffins into the benzol series.

Here, in the United States, there are several methods of making illuminating gas from petroleum by passing it into heated retorts. I was informed by Mr. John Lerltus, of East Boston, that the tar from these gas-works resembled very much the tar from coal-gas. I examined a specimen of this tar and found that it did contain the benzol compounds, but not either phenol or cresol.

This points very distinctly to the decomposition of the normal paraffins of petroleum into the benzol compounds [fol. 809] on a rather large scale. It seems to me that it might lead to the obtention of benzole by passing petroleum benzine (which sells here at about 7 to 8 cents per gal.) through tubes heated to the proper temperature. In connection with the manufacture of gas the yield, even if quite small, might be made to pay. At all events the new methods of gas-making will still afford us a source for benzole and its derivatives.—I am, &c.,

S. Cabot, Jun.

Boston, August 29, 1877.

[fol. 810] PETITIONER'S EXHIBIT No. 113

The Analyst, Including the Proceedings of the "Society of Public Analysts," a Monthly Journal for the Information of Those Interested in the Purity of Food and Drugs and in General Analytical and Microscopical Research

Edited by G. W. Wigner, F.I.C., F.C.S., London and America, one of the Hon. Secretaries of the Society of Public Analysts, and J. Muter, Ph.D., F.I.C., F.C.S., Vice-President of the Society of Public Analysts

Vol. VI

1881

London: Published for the Proprietors by Messrs. Bailliere, Tindall & Cox, King William Street, Strand, W.C.

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(Pages 177 to 180)

The Analyst, October 1881

Society of Public Analysts

The Country Meeting of this Society was held on the 6th September at York, during the British Association Meet-

[fol. 811] ing. In the absence of the President, Dr. Wallace took the chair.

The ballot papers were opened by Mr. Jarmain and Mr. Baynes, and the following gentlemen were declared to be duly elected:—C. M. Blades, Analytical Chemist, Northwich; C. Girard, Public Analyst for Paris; C. T. Kingzett, F.C.S., F.I.C., Analytical Chemist, London.

The following gentleman was proposed for election:—W. J. R. Simpson, M.D., Aberdeen.

Mr. Allen read a paper "On the Relative Proportions of Olefines in Shale and Petroleum Products."

The chairman, in addressing a few remarks to the meeting, congratulated the Society on the good work they had done during the past year in respect of the scheme they had published of water analysis; and while speaking of it with great eulogium, expressed a hope that the Society would continue some similar labours in a new direction. He thought it would be worth while if the Society were to consider as to some new subject to be recommended to the Council for reference to a committee, who should be requested to frame a new series of instructions which would be of assistance to Public Analysts.

It was suggested that a good subject would be the preparation of a catalogue of the re-agents, which ought to be found in the laboratory of a Public Analyst, the sources from whence they can be best procured, and if requisite the best modes of their manufacture, the tests for their purity, and methods of purification where requisite.

On the Relative Proportions of Olefines in Shale and Petroleum Products

By Alfred A. Allen

Read Before the Society of Public Analysts, at York, on 6th Sept., 1881

In a previous Paper I have shown that some of the commercial products obtained by the distillation of bituminous shale differ from the parallel series of products derived from petroleum. As far as the action of strong nitric and sulphuric acids is concerned, this difference is fully recognized by those familiar with the products in question, and has been rightly attributed to the different proportions of

olefines contained in them. The method of treatment of the hydrocarbon with fuming nitric acid, fuming sulphuric acid, and caustic soda used successively, is practically a process for the estimation of the paraffins, the hydrocarbons of all other series being destroyed or converted into soluble products.

[fol. 812] One of the best known and most characteristic properties of the olefines or hydrocarbons of the ethylene series is the readiness with which they enter into combination with bromine to form additive compounds of a stable and definite character. The paraffins, or hydrocarbons of the marsh gas series, on the other hand, do not form additive compounds with bromine, and are practically unaffected by it under the ordinary conditions of experiment.

Combination with bromine has long been used for assaying coal gas for the proportion of ethylene and allied hydrocarbons contains- in it, and has been previously employed for the examination of shale-products. I*t* have, however, been unable to learn the precise manner in which it has been used for the latter purpose. At first I met with considerable practical difficulty in applying it quantitatively, chiefly owing to the solubility of the excess of bromine in the brominated rendering it difficult to observe the end of the reaction. Hence it may be of interest to describe the plan which I ultimately adopted, and by which such numerical results as I shall lay before you have been obtained.

A solution of hypobromite of sodium is prepared by measuring out 40 c.c. of bromine, gradually adding solution of caustic soda (avoiding any rise of temperature) till the liquid is slightly alkaline and of a light yellow colour, and then diluting the liquid with water to 1 litre. The strength of this solution is then ascertain- by measuring out 20 c.c., diluting with about 150 c.c. of water, in a porcelain dish, adding a strong solution of pure iodide of potassium, and then acidulating the mixture with hydrochloric acid. The iodine set free is then titrated with decinormal solution of sodium thiosulphate (hyposulphite, 24·8 grammes of crystallized $Na_2S_2O_3$ per litre).*

* It is desirable to ascertain the strength of the hypobromite solution every few days.

Five grammes or 5 c.c. of the sample of mixed hydrocarbons to be tested is next placed in a small tapped separator, or Mohr's burette with a glass tap, 5 c.c. of the bromine solution added, the mixture acidulated with dilute hyrdochloric acid, and well agitated. The liberated bromine will be dissolved by the hydrocarbon, and in most cases will combine with it to form a bromide, or be acted on with production of a bromo-substitution product. In either case, the red colour of the free bromine will disappear par- [fol. 813] tially or completely. If standing a minute or two the layer of hydrocarbon is found to have a marked red or yellow colour, the bromine treatment is at an end, but otherwise a further addition of a known measure of hypobromite solution is made and the agitation repeated.†

Excess of bromine solution having been added, as indicated by the permanent red or yellow colour of the hydrocarbon layer, the mixture is allowed to rest a few minutes to permit the aqueous liquid to separate. In some cases this occurs readily, but in others the brominated oil adheres to the sides of the vessel, and, if of about the same denisty as the aqueous liquid, only separates with great difficulty. In such cases it is desirable to add sufficient petroleum spirit to cause the hydrocarbon to rise readily to the surface.‡

Complete separation of the two layers having been effected, the aqueous liquid is run off through the tap into a porcelain basin, and the brominated oil is shaken with sufficient solution of caustic soda to render it colourless. The soda solution is run off into the porcelain basin, the oil washed by agitation with a little water and the washings run off in their turn. Iodide of potassium is then added to

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† In the analysis of shale-naphtha 5 c.c. of the sample often requires an addition of 25 c.c. of bromine solution to effect complete bromination.

‡ This plan never fails. The petroleum spirit employed may be ordinary commercial "benzoline," but it must be previously agitated with enough bromine water to render it permanently coloured, and then with sufficient caustic soda to decolourize it. Treated in this manner it is rendered indifferent to bromine.

the liquid in the basin, and sufficient hydrochloric acid to render it distinctly acid. The mixture is then titrated with the sulphate in the same manner as the bromine solution. The quantity of bromine thus found is the excess employed, and if deducted from the total quantity present in the volume of hypobromite solution added to the oil, the weight of bromine will be found which is required to combine with the quantity of hydrocarbon taken for the experiment.

When a solid hydrocarbon, such as vaseline or paraffine, is to be examined, 2 grammes of it should be dissolved in the smallest necessary quantity of petroleum spirit (previously brominated), and the solution so obtained treated in the usual manner.

[fol. 814] Operating in the manner above described the method gives very constant results. The following figures show the proportion of bromine which the author found to react with samples of representative commercial products, consisting wholly or chiefly of hydrocarbons. In nearly all cases the numbers given are the mean of two or more concordant experiments.

Substance	Specific gravity at 15.5° C.	Grammes of bromine combining with 100 grms. of sample	Percentage of bromine in product
Naphthas—			
1. Gasolene from Shale	.665	67.1	41.6
2. Gasolene from Petroleum	.652	5.1	4.8
3. Shale Naphtha	.718	94.9	48.7
4. Petroleum Naphtha	.690	10.0	8.8
5. Benzol	.876	36.2	26.6
Burning Oils—			
6. From Shale	.801	38.7	27.9
7. From Shale	.806	36.4	26.7
8. From Petroleum	.800	17.2	14.7
Lubricating Oils—			
9. From Shale	.889	56.4	36.0
10. From Shale (Bloomless)	.875	45.3	31.2
11. From Petroleum (Spindle Valvoline)	.862	21.6	17.7
12. From Petroleum (Oleonaphtha)	.905	31.8	24.1
13. Rosin Oil	.973	45.3	31.2
14. Refined Rosin Oil	.978	41.7	29.9
Solid Products—			
15. Vaseline	....	19.7	16.5
16. Paraffine Wax	....	....	....

From these results it will be seen that there is in each case a striking difference between the proportion of bromine assimilated by any of the shale-products and the quantity which combines with the parallel product from petroleum. Thus, while the shale naphhta took up nearly its own weight of bromine, the petroleum naphtha combined with only 10 per cent., and the gasolenes, burning oils and lubricating exhibit similar but somewhat less striking differences. Benzol does not give a satisfactory result, the reaction with bromine occurring slowly instead of instantaneously, as is the case with the shale of petroleum products.

Owing to the complex character of commercial hydrocarbon products, a determination of the amount of bromine combining with them does not give the means of calculating the actual percentage of olefines contained in them. If, however a fraction of constant boiling point were pre- [fol. 815] pared, and its vapour density ascertained, its mean combining weight could thence be deduced, and then a determination of its power of assimilating bromine would give a means of obtaining a close approximation to the proportion of olefines contained in the fraction. This suggestion of course assumes the absence of hydrocarbons of the acetylene series and other bodies simulating the olefines in their reaction with bromine.

Broadly speaking, the relative proportion of olefines present in two products of similar density and boiling-point is pretty exactly indicated by the power of assimilating bromine; and as the shale-products combine with from twice to ten times as much bromine as the parallel products from petroleum, it may be safely assumed that the former products are far richer in olefines than are the latter.

My acknowledgments are due to Mr. W. S. Gunn for the valuable assistance he has afforded me in ascertaining the bromine taken up by various products.

Inland Revenue Report

The twenty-fourth report of the Inland Revenue Commissioners has just been issued, and we take from it the following report by the Principal of the Laboratory:—

The number of samples examined during the year ended 31st March last was 18,014, which is 2,901 in excess of the

previous year. The increase is principally due to the operation of the new beer duty, and caused a great strain upon the department during the latter half of the year.

Under the Inland Revenue Act, 1880, which abolished the duty on malt, and imposed an equivalent tax on beer, 1,332 samples have been examined. Most of these were for the determination of the original gravity, to confirm or otherwise the gravity declared by the brewer or that found by the officer. As the samples examined at this laboratory are usually taken when the wort is in a partially fermented state, the conditions for obtaining an average sample are more favourable than before fermentation has commenced. The detection of sugar which has been illegally added to wort with the view of increasing the gravity has entailed a considerable amount of work of a kind requiring much skill and experience. We have so far successfully dealt with this form of fraud, and several prosecutions have been instituted against brewers, and a conviction obtained in [fol. 816] each case. There appears to be a strong tendency among small brewers, more especially in the Midland Counties, who, through want of skill or attention, fail to get a produce of worts corresponding to the charge from materials, to use a quantity of sugar without entering it upon the brewing paper, and thereby escape payment of duty on a deficiency of produce from the malt. The percentage of samples in which the true gravity has exceeded that declared has been very considerable.

As the mode of charging the duty on worts called into use a very large number of saccharometers intended as standards, and for general use by officers, the work of verifying many of these instruments fell upon this department. The result led to the rejection of many imperfect instruments.

Twenty-six samples under the Sale of Food and Drugs Act have been referred to us by direction of the magistrates. They comprised milk, butter, coffee, mustard, and tincture of quinine. In twelve instances our certificate agreed with, and in fourteen it differed from, that of the public analyst. In the case of two samples of butter said to contain foreign fat, our results showed that they were genuine butter. In another case a portion of the butter analyzed by the defendant's analyst was sent here along with the sample in the hands of the——

[fol. 817] PETITIONER'S EXHIBIT No. 114

The Chemical News and Journal of Physical Science, with Which is Incorporated the "Chemical Gazette," a Journal of Practical Chemistry in all its applications to Pharmacy, Arts and Manufactures

Edited by William Crookes, F.R.S., &c.

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MDCCCLXXXIV.

(Page 197)

On the Fluid Hydrocarbons Obtained by the Compression of Petroleum Gas

By Greville Williams, F.R.S.

When the gaseous hydrocarbons produced by subjecting petroleum to a high temperature are compressed into cylinders, as in the Pintsch system, so much employed for lighting railway carriages, a volatile fluid is condensed contain- [fol. 818] ing benzene, toluene, and certain olefines. I have been engaged in the examination of this mixture of hydrocarbons since October, 1882. As I find that Dr. Armstrong is working on the same subject, I think it desirable to give a brief outline of some of the results which I have obtained up to the present time.

The plan I have adopted for the separation of the olefines from the benzene and its homologues is as follows:—I first pass the vapours of the hydrocarbons through a powerful rectifying column. The portions distilling below 66° C. I put aside for the preparation of the olefines which I require for conversion into hydriodates, in order to continue work commenced by me in 1862 (Journ. Chem. Soc., xv., 359). The portions distilling above 66° C. I use for the preparation of benzene and toluene. The olefines may be separated from the latter by agitating the hydrocarbons with a cold solution of permanganate of potassium, as shown by Berthelot; or, preferably, by distilling from dilute nitric acid. By this last method nitro-compounds are produced, which are now under examination.

The nitric acid process properly carried out yields results of considerable precision, the amounts of benzene and toluene obtained in repeated experiments being within one per cent of each other.

The specimens of the hydrocarbons from the various stations where the Pintsch process is carried out differ considerably in the amount of benzene and toluene they contain. Seven specimens with which I was favoured by Mr. Rickman, the Managing Director of the Pintsch Company, gave me the annexed numbers:

Specimen	Specific gravity	Percentage of benzene & toluene
A	0.850	65.6
B	0.835	54.2
C	0.840	52.0
D	0.830	45.2
E	0.840	44.4
F	0.800	37.8
G	0.760	24.6

[fol. 819] PETITIONER'S EXHIBIT No. 115

Allen's Commercial Organic Analysis, a Treatise on the Properties, Modes of Assaying, and Proximate Analytical Examination of the Various Organic Chemicals and Products Employed in the Arts, Manufactures, Medicine, etc., with Concise Methods for the Detection and Estimation of Their Impurities, Adulterations, and Products of Decomposition

Volume III

Hydrocarbons, Bitumens, Naphthalene and Its Derivatives, Anthracene and its Associates, Phenols, Aromatic Acids, Gallic Acid and its Allies, Phthalic Acid and the Phthaleins, Modern Explosives

By the Editors and the Following Contributors: F. C. Garrett, W. P. Dreaper, Edward Horton, A. Marshall

Fourth Edition. Entirely Rewritten

Edited by W. A. Davis, B. Sc., A. C. G. I., Formerly Lecturer and Assistant in the Chemical Research Laboratory, City and Guilds College, Imperial College of Science and Technology, London, and Samuel S. Sadtler, S. B., Vice-President of the American Electro-Chemical Society; Member American Institute of Chemical Engineers

Philadelphia: P. Blakiston's Son & Co., 1012 Walnut Street: 1910

(Pages 117, 12-13, 106-110, 115-117)

Hydrocarbons

By F. C. Garrett, D. Sc.

The hydrocarbons (i. e., those compounds which contain only carbon and hydrogen) fall into two great classes:

A. The Aliphatic or Acyclic Hydrocarbons (the paraffins, [fol. 820] acetylene, etc.) in which the carbon atoms are linked together in open chains.

B. The cyclic hydrocarbons (benzene, naphthalene, etc.) in which some or all of the carbon atoms form a closed chain or ring.

The Aliphatic Hydrocarbons

This large class is subdivided into several groups, according to the ratio between the numbers of carbon and hydrogen atoms in the molecule, the only important ones being the paraffins, the olefines, the acetylenes, and the diolefines.

The Paraffins.—This, the largest of all the groups, includes those hydrocarbons in which the carbon atoms are united only by single linkages (hence called saturated hydrocarbons), and which consequently contain the largest possible amount of hydrogen, the general formula being C_nH_{2n+2}. Its members are formed when carbonaceous matter decays or is decomposed by heat in the absence of oxygen at relatively low temperatures and consequently are found in the emanations from marshes, the gases escaping from ponds, the "blowers" of the coal pits, and in coal-gas, coal-tar, shale oil, etc., as well as in the natural gas of the petroleum districts and in petroleum—particularly that of Pennsylvania; while the higher members ($C_{35}H_{72}$, for example) occur as the minerals ozokerite, hatchettite, ceresine, etc.

Although the first three members of the series each exist in one form only, there are two butanes, three pentanes, and five hexanes, all of which are known, while the number of isomerides of the higher homologues theoretically possible is enormous, and for such a substance as $C_{13}H_{28}$ no less than 802 formulæ can be devised. Of the higher paraffins comparatively little is known, few having been obtained in a state of purity, and it is probable that in most cases even the m. p. and b. p. have not been ascertained with any degree of accuracy.

The following table gives the physical constants of the normal paraffins, and is taken (with some additions) from Richter's "Organische Chemie" (11th edition, 1909).

[fol. 821]

	Formula	M. p.	B. p. at 760 mm.	B. p. at 15 mm.
Methane	CH_4	—184°	—164°	.....
Ethane	C_2H_6	—172°	— 84°	.....
Propane	C_3H_8	.....	— 45°	.....
Butane	C_4H_{10}	.....	1°	.....
Pentane	C_5H_{12}	.....	38°	.....

	Formula	M. p.	B. p. at 760 mm.	B. p. at 15 mm.
Hexane	C_6H_{14}	.....	71°	.....
Heptane	C_7H_{16}	.....	98.4°	.....
Octane	C_8H_{18}	.....	125.5°	.....
Nonane	C_9H_{20}	— 51°	149.5°	.....
Decane	$C_{10}H_{22}$	— 32°	173°	.....
Undecane	$C_{11}H_{24}$	— 26.5°	194.5°	.....
Dodecane	$C_{12}H_{26}$	— 12°	214°	.....
Tridecane	$C_{13}H_{28}$	— 6°	234°	.....
Tetradecane	$C_{14}H_{30}$	+ 5.5°	252.5°	.....
Pentadecane	$C_{15}H_{32}$	+ 10°	270.5°	.....
Hexadecane	$C_{16}H_{34}$	+ 18°	287.5°	.....
Heptadecane	$C_{17}H_{36}$	+ 22.5°	303°	170°
Octadecane	$C_{18}H_{38}$	+ 28°	317°	181°
Nonadecane	$C_{19}H_{40}$	+ 32°	330°	193°
Eicosane	$C_{20}H_{42}$	+ 36.7°	.....	205°
Heneicosane	$C_{21}H_{44}$	+ 40.4°	.....	215°
Docosane	$C_{22}H_{46}$	+ 44.4°	.....	224°
Tricosane	$C_{23}H_{48}$	+ 47.7°	.....	234°
Tetracosane	$C_{24}H_{50}$	+ 51.1°	.....	243°
Heptacosane	$C_{27}H_{56}$	+ 59.5°	.....	270°
Hentriacontane	$C_{31}H_{64}$	+ 68.1°	.....	302°
Dotriacontane	$C_{32}H_{66}$	+ 70.0°	.....	310°
Pentatriacontane	$C_{35}H_{72}$	+ 74.7°	.....	331°
Octatriacontane	$C_{38}H_{78}$	+ 79.4°	.....	.....
Hexacontane	$C_{60}H_{122}$	+ 102°	.....	.....

The paraffins are not attacked by chlorine in the dark, nor are they absorbed by bromine or by sulphuric acid, and so can easily be separated from the other aliphatic hydrocarbons; they are hardly attacked at all by fuming nitric acid or by chromic acid in the cold, although even dilute nitric acid converts normal hexane, heptane, and octane into nitro-paraffins on warming. (See Konowalow, Compt. rend., 1892, *114*, 26; Ber. 1895, *28*, 1852; Worstall, Amer. Chem. J., 1898, *20*, 202; 1899, *21*, 210; Francis and Young, Trans., 1898, *73*, 928.) In daylight chlorine attacks them vigorously giving substitution products, bromine less readily, and iodine has no action.

Detection and Estimation of Paraffins.—Paraffins in the [fol. 822] vaporous or gaseous state can be separated from

hydrocarbons of the olefine and acetylene series by treatment in the dark with excess of bromine. The paraffins remain unaffected, while the unsaturated hydrocarbons are converted into liquid bromine compounds. The same principle is also applicable to liquid mixtures of paraffins and olefines. The unchanged paraffins may be separated from the olefine bromides by distillation in a vacuum.

When paraffins are heated with bromine and water for some time in sunlight, they are converted into bromo-substitution compounds, half the bromine which enters into action being afterwards found as hydrobromic acid. This behaviour may, under favorable circumstances, be employed for their recognition and quantitative estimation.

Liquid paraffins may also be separated from hydrocarbons of other series by treating the mixture first with sulphuric acid, so long as the acid becomes coloured, and then with fuming nitric acid, avoiding rise of temperature. Other substances are oxidized, or converted into nitro-compounds which remain dissolved by the acids or are much less volatile than the unaltered paraffins. After washing with water, drying over caustic potash, and certification over sodium, a distillate of pure paraffins is obtained. A practical use of this principle is sometimes made in analysis.

The Olefines, C_nH_{2n}

The olefines closely resemble the paraffins in their physical properties, and are converted into them by nascent hydrogen; containing less hydrogen, they are "unsaturated compounds," and hence unite very readily with bromine (even in the dark), the halogen acids, concentrated sulphuric acid, etc.

Estimation of Olefines.—The only methods practically available for the direct and accurate estimation of olefines, when in admixture with hydrocarbons of other series, are based on the facility with which they unite with bromine, or their absorption by fuming sulphuric acid.

For the estimation of the gaseous olefines, as existing in coal-gas, a known measure of the gas is introduced into a graduated Cooper's tube, care being taken that the water which is displaced has been previously saturated with gas of the same quality. Bromine is then dropped into the

water which remains in the curved part of the tube, the tube closed with a stopper or the thumb, and the contents well agitated.

[fol. 823] On opening the tube under water, the diminution of the volume of the gas will indicate that olefines have been absorbed, and, on observing the water, oily globules of $C_2H_4Br_2$ etc., will be perceived. These should be red or yellow in colour; if colourless, more bromine must be added and the agitation repeated. The tube being again opened under water, a small piece of sodium hydroxide is added to absorb free bromine and the tube agitated once more. The tube is then immersed in a cistern having glass sides, so that the volume of the residual gas can be read off when the water in the cistern is on the same level with that in the tube. The loss of volume, duly corrected, if necessary, for temperature and pressure, gives the hydrocarbons absorbable by bromine.

Satisfactory estimations of olefines can also be made by means of Hempel's gas-burette or Lunge's nitrometer. Hempel (Methods of Gas Anal.) states that the sulphuric acid method is the most accurate.

When the proportion of olefines is small, a known measure of the gas can be caused to bubble through a solution of bromine in carbon disulphide.

For the estimation of the olefines in liquid hydrocarbons the bromine method is still available, but the method of operating must be modified. The following modification of the process of Mills and Snodgrass (Vol. 2) has been extensively employed in Allen's laboratory and found very useful for the examination of commercial products from shale and petroleum. An approximately decinormal solution of bromine is made by dissolving 2 c.c. of bromine in 750 c.c. of recently distilled carbon disulphide. This solution, which keeps well in the dark, is rendered anhydrous by the addition of some lumps of dry calcium chloride. An accurately weighed or measured quantity of the dry hydrocarbon, weighing between 0.3 and 1.0 grm., or a volume of a solution of the oil in carbon disulphide containing a known weight of the hydrocarbon, is then placed in a perfectly dry stoppered flash or separator, the solution diluted, if necessary, with carbon disulphide (kept over calcium chloride) to about 25 c.c., and then 25 c.c. of the carbon disulphide solution of bromine added. The flask is then

closed, and the contents agitated. If the liquid is distinctly red, sufficient bromine has probably been added, but should the solution be nearly or quite decolourised, a further addition of a known measure of the bromine solution should be made without delay. The flask is then at once [fol. 824] placed in the dark and kept there for a quarter of an hour, when an excess of an aqueous solution of potassium iodide is poured in, the contents agitated, the flask removed to a light place, and the solution titrated with a decinormal solution of sodium thiosulphate (24.8 grm. of crystallised salt per litre). The end of the action is indicated by the decolourisation of the carbon disulphide, and is rendered sharper by adding a few drops of starch solution toward the end of the titration.

25 c.c. of the carbon disulphide solution of bromine are then placed in a similar flash, potassium iodide solution added, and the titration with thiosulphate conducted as before. The difference between the volume of standard thiosulphate now required and that previously employed for the titration in presence of the hydrocarbon is the measure of thiosulphate corresponding with the bromine which has combined with the unsaturated hydrocarbons present. 1 c.c. of decinormal thiosulphate corresponds with 0.008 grm. of bromine. The bromine solution keeps for a considerable time without change, and hence the verification of its strength is only occasionally necessary.

It is absolutely necessary not to expose the hydrocarbon to the action of bromine in presence of strong light; even a very moderately diffused daylight is prejudicial, but gaslight has no sensible effect. Fifteen minutes should be allowed for the completion of the action. If much exceeded, secondary changes are liable to occur, which give results in excess of the truth, more or less hydrogen bromide being usually produced, the amount increasing with the time allowed for the action. On the other hand, the combination with bromine is sometimes not completed immediately. McArthur (J. Soc. Chem. Ind., 1888, 7, 65) points out that moisture must be rigorously excluded, the bromine added must be twice the quantity required for absorption (ascertained by a preliminary experiment), and the oil solution must be diluted with carbon disulphide to three times the volume of the bromine solution that is to be added.

The foregoing process gives tolerably concordant results, and was adopted by Allen in place of a method described by himself, in which the bromine was employed in aqueous solution. In its simplest form this process is conducted exactly in the manner just described, except that approximately decinormal aqueous bromine is used, instead of a carbon disulphide solution of that element, and the potas- [fol. 825] sium iodide solution is added directly after the oil has been thoroughly shaken with the bromine water. If the bromine compounds formed are viscous and adhere strongly to the sides of the flask, so as to hinder the action of the bromine water, a few centimetres of carbon disulphide may be added, by which the oils will be dissolved, and may be brought in contact with the bromine water by agitating. This method gives fairly constant results, but they do not represent simply the bromine assimilated by the unsaturated hydrocarbon, etc., of the sample, as oxidation also occurs to a very sensible extent. The results obtained are therefore in excess of those given by the carbon disulphide process, but they are fairly comparative, and for works-assays of shale and petroleum products the method will be found of service.

Owing to the complex character of commercial hydrocarbons, an estimation of the amount of bromine combining with them does not give the means of calculating the percentage of olefines present. If, however, a fraction of constant b. p. be prepared and its vapour density ascertained, its mean combining weight can be deduced, and an estimation of its power of assimilating bromine gives a means of obtaining a close approximation to the proportion of olefines contained in the fraction. This suggested method assumes that the fraction consists essentially of paraffins and olefines. Any admixture of hydrocarbons of other series would further complicate the problem.

On this account it is preferable in practice to express the results of titrations as bromine absorptions; that is, in grams of bromine assimilated by 100 grm. of the oil. If a known volume of the sample has been employed, the number of grams of bromine taken up by 100 c.c. must be divided by the density of the sample to ascertain the bromine assimilated by 100 grm.

It must be borne in mind that, besides olefines, many other substances, both hydrocarbons and oxygenated substances assimilate bromine, and hence the "bromine absorption" of a complex mixture arises from several sources. Nor does the bromine absorbed by substances other than olefines bear a constant relation to their molecular weight. Thus the hydrocarbons of the acetylene series absorb either Br_2 or Br_4, and the latter proportion is also assimilated by terpenes. Oleic acid combines with Br_2, linoleic acid with Br_4, and phenol with Br_6, a bromo substitution product [fol. 826] being formed in the last case. The results given by these substances are described in the sections on oleic acid, turpentine oil, phenol, etc.; and estimation of the bromine absorptions of shale and petroleum products, rosin oil, and resins will also be found duly recorded.

It is possible to ascertain the iodine absorption of hydrocarbons by Hübl's method, which gives results comparable with those obtained by bromine if the former be multiplied by the factor 0.63. The process is, however, not well adapted for the examination of hydrocarbons, as the action may not be complete in less than twenty-four hours.

The Acetylenes, C_nH_{2n-2}

The members of this group are usually oily liquids of rather higher b. p. than the corresponding paraffins; they are, of course, unsaturated compounds, containing a triple linkage, and react with hydrogen, the acids, halogens, etc., in very much the same manner as the olefines. Their most characteristic property is the great readiness with which they react with ammoniacal solutions of cuprous or silver salts, forming compounds such as $C_2H_2.Cu_2O$ which are almost always thrown down as precipitates. By this property they can be distinguished and separated from all other hydrocarbons.

The cuprous solution is prepared by treating copper turnings in a separator with strong ammonia in presence of a limited quantity of air, until the blue liquid first formed has become colourless. The regeant is then run from the tap into a U-tube fitted with a tube bent twice at right angles, the open end of which dips under water, so as to prevent contact of air. On passing a gas through the

cuprous solution, a yellow or red precipitate will be produced if acetylenes be present. If the precipitate be filtered from the liquid and treated with strong hydrochloric acid, the acetylene will be liberated. This behaviour furnishes a mean of isolating acetylene and its homologues in a condition of purity. On treating the cuprous compound with aqueous ammonia and zinc, the corresponding olefine will be produced, and may be identified by the proportion of bromine with which it unites.

The silver derivatives of the acetylenes may be obtained by substituting an ammoniacal solution of silver nitrate for the cuprous solu-

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also principally converted into volatile compounds. Slow [fol. 827] heating will sometimes produce volatilisation with little or no change. The nature and proportions of the substances obtained will be dependent on the character of the substance distilled, the temperature of the retort, and other conditions; when the heat is moderate, paraffins are chiefly produced; but as the higher members of this series readily split up into lower members and olefines, the latter are nearly always present. By further degradation acetylenes are formed, while benzene and its homologues contain a still smaller proportion of hydrogen.

When the temperature is high, hydrogen, acetylene, benzene, and naphthalene are the chief unoxygenated products. Thus, coal being distilled at a high temperature for the manufacture of coal-gas, the condesable hydrocarbons consist chiefly of benzene and its homologues, naphthalene, etc. At a somewhat lower temperature the hydrogen and acetylene disappear, together with most of the naphthalene, while chrysene and a larger proportion of benzene are formed.

At a dull red heat, such as is employed for the distillation of bituminous shale, the liquid products are almost free from benzene and naphthalene, while little or no hydrogen or acetylene is present in the gases. On the other hand, the distillate is rich in paraffins and olefines with some anthracene and chrysene; the oxygenised and nitrogenised products consist chiefly of substances of the formula $C_nH_{2n-7}OH$, and other phenolic compounds, and

bases of the formula $C_nH_{2n-5}N$ (pyridine bases), although the corresponding series, C_nH_{2n-6}—i. e., benzene and its homologues—is almost wholly absent.

When wood is subjected to dry distillation, the volatile products are practically free from compounds of nitrogen and sulphur. The watery portion of the distillate from wood, peat, and lignite has an acid reaction, owing to the presence of acetic acid. In other respects the products of the distillation of wood, as ordinarily conducted, are a mixture of low- and high-temperature products.

When the temperature of the distillation is low, a large yield of liquid products is usually obtained, together with a small yield of gas of high illuminating power. At a high temperature a maximum production of gas of low illuminating power results, while the proportion of liquid products is small. The higher the temperature of the retort, the larger the percentage of solid carbonaceous residue (coke or charcoal) left in it.

[fol. 828] The three cases afforded in practice by the treatment of coal, shale, and wood may be regarded as typical of the changes attending the destructive distillation of organic substances, though others, such as bone, rosin, and oil, yield special products of some practical interest. Too much stress cannot be laid on the fact that the nature of the products depends not only on the nature of the substance treated, but also on the circumstances under which the operation is conducted with regard to temperature and other conditions.

The following table indicates the general nature of the more prominent volatile organic products of the dry distillation of coal (for the manufacture of illuminating gas), bituminous shale, and wood, as the processes are carried on in practice. To facilitate comparison, the leading constituents of American petroleum are shown in juxtaposition:

Organic products	Coal	Bituminous shale	Wood	Petroleum
Hydrogen	Large	Traces	Large	Present
Gaseous Hydrocarbons:				
Methanes	Large	Large	Large	Present
Olefines	Large	Large	Considerable	Present
Acetylenes	Present	None		
Liquid and Solid Hydrocarbons				
Liquid paraffins	Small	Large	Absent	Very large
Solid paraffins	Traces	Considerable	Present	Moderate
Liquid olefines	Small	Very large		Considerable
Liquid pseudolefines				Present
Liquid acetylenes	Present	Present		
Benzenes	Large	Trace	Moderate	Present
Napthalene	Large	None	Moderate	None
Anthracene	Moderate	Trace		Present
Chrysene	Moderate	Considerable	Present	Present
Oxygenated Bodies:				
Acetic acid	Present	Present	Large	
Methyl alcohol	None		Considerable	
Phenols	Large	Considerable	Moderate	
Hydroxyphenols (creosote)		Large	Large	

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Organic products	Coal	Bituminous shale	Wood	Petroleum
Nitrogenised Bodies:				
Ammonia	Considerable	Considerable	None	
Aniline bases	Present	None		
Pyridine bases	Considerable	Considerable		
Acridine	Present			
Carbazole	Present			
Sulphur Compounds	Present	Present	None	Present

It will be seen from this table that the products of the distillation of each of the raw materials contain certain characteristic bodies. Thus, oxygenated products are found most largely in the products of the distillation of wood; paraffins are especially characteristic of petroleum; olefines, and, to a lesser extent, paraffins, of the distillation of shale; is used in practical work, and a portion is then flowed over the surface of a slab of marble or glass, [fol. 829] 4″x5″x1″ thick. After standing 24 hours at 25°, the film upon the stone must be decidedly sticky when tested with the fingers, and must adhere to the stone so that it cannot be pulled off.

Volatile Substances.—100 grm. of the material is placed in a 6-oz. tubulated glass retort, with the bulb of an accurate thermometer in the same. Heat is now applied so that the temperature rises at the rate of 10° per minute to 700° F. The distillate, if any, is regarded as the amount of volatile substances in the material. The residue is examined by the New York Testing Laboratory float for consistency, and compared with the results obtained upon the original material by this test.

Petroleum and Shale Products

The parallel products obtained by the distillation of crude petroleum and the oil or tar from bituminous shale (page 16) present a marked similarity in general character, though differing notably in certain respects. As a rule, the treatment of petroleum is a much simpler operation than the manufacture of marketable products from crude shale oil, but, broadly speaking, the same method of treatment is applied to both of the raw materials. The process employed consists essentially in fractional distillation, and treatment of the separate fractions successively with sulphuric acid and caustic soda, to remove bodies of acid and basic character and to destroy the less stable hydrocarbons. The less volatile portions deposit paraffin wax on cooling. The following table shows in parallel columns the character and quantities of the products obtained in first-class works from crude American petroleum of 0.800 sp. gr. and Scotch shale oil produced at the works of the Broxburn Oil Company:

Products	From petroleum		From shale oil	
	Sp. gr.	Percentage	Sp. gr.	Percentage
Cymogene and rhigolene	.590 to .625	Very small		Very small
Gasolene	.636 to .657	1.0 to 1.5		
"C" naphtha ("benzin-naptha")	.700	5 to 10	0.730	5
"B" naphtha	.714 to .718	2.5		
"A" naphtha ("benzin")	.725 to .737	2.0 to 2.5		
Kerosene or burning oil	.802	50 to 70	0.800 to .810	37
Lubricating oil	.875	2.5 to 17	0.885	17
Paraffin wax		2		13
Coke, gas, and loss		8 to 10		28

The yield of burning oil from any sample of petroleum may be increased nearly 20% with corresponding diminu- [fol. 830] tion of heavier products by a modification of the distillation by which the hydrocarbons of higher b. p. are changed by dissociation into bodies of lower b. p. This process, technically known as "cracking," was discovered by accident in an American refinery about 40 years ago, and is now generally adopted since an increase in the burning oil is the most valuable result to the refiner. The chemistry involved in the change is not thoroughly understood. It is carried out in practice by arranging the distilling apparatus so that the hydrocarbons are condensed and fall back in drops upon the much hotter body of the liquid in the still. By this action the condensed oils become overheated and changed. Burning oils obtained by this method are different from, and somewhat inferior to, those produced by normal distillations, but the process, as noted above, is very much in vogue.

The Abruzzo bitumen is said to yield on distillation:

	%	Sp. gr.	Flashing point
Burning oil	15	0.850	54.5°
Intermediate	33	0.945(?)	121.1°
Lubricant	16½	0.990(?)	157.2°

The products from Russian petroleum are very different in both density and percentage from those yielded by the American oil (see pages 108, 128 and 129). Rangoon tar of 0.885 sp. gr. gives, on an average, the following proportions of refined products: Burning oil (sp. gr. 0.832), 30%; lubricating oil (sp. gr. 0.901), 51%; and paraffin scale (melting at 51.4°), 10.7%.

The products obtained by the distillation of ozokerite have already been described.

The number of products into which the more volatile portions of shale oil and petroleum are fractionated varies considerably according to the practice of the works, but gasolene and the more volatile products are obtainable from shale oil equally with petroleum. The only commercial product obtainable from petroleum having no analogue among the products from shale oil is the substance known as vaseline. Sadtler (Ind. Org. Chem.) quotes the follow-

ing table from Wagner's Jahresbericht, 1886, for the percentage of petroluem distillation on the large scale:

[fol. 831]

Crude oil	Benzin and volatile oils	1st quality burn. oil	2d quality burn. oil	Residuum
Pennsylvania	10 to 20		60 to 75	5 to 60
Galicia	3 to 6		55 to 65	30 to 40
Alsace			35 to 45	55 to 60
Roumania	4		60 to 70	25 to 35
Baku (Bibi-Eibat)	10.5	40	13.5	36
Baku (Balakhan)	5 to 6	27 to 33	5.6	50 to 60

The more volatile products from petroleum are briefly described on page 111. The similar fractions from shale oil closely resemble the petroleum products in their physical character, but they contain a much larger proportion of olefines. This chemical distinction had been traced by Allen in each of the parallel products from American petroleum and shale oil, and is the cause of some curious differences in the behaviour of these substances as solvents and with chemical reagents.

The following table gives a general idea of the chemical composition of the leading commercial hydrocarbon products deprived from bituminous shale and American petroleum. Of course, the quantitative composition is liable to considerable variation, and hence must not be interpreted too strictly. The general and analytical characters of the products named in the table are described in the succeeding sections. The hydrocarbons from distillation of coal do not admit of parallel comparison with those from petroleum and shale.

Product	Bituminous shale	American petroleum
Naphtha	At least 50 to 60% of heptene and homologues. The remainder as paraffins. No trace of aromatic hydrocarbons	At least 75% of heptane, and homologues. The remainder apparently olefines, with distinct traces of aromatic hydrocarbons
Kerosene or burning oil	50 to 80% or more of the higher olefines. The remainder paraffins	50 to 80% of higher members of the methane series. The remainder chiefly olefines.
Lubricating oil	Chiefly olefines, with some polymerised members of the acetylenes	A large proportion of higher olefines, but less than in corresponding shale product
Vaseline	No such product	Chiefly higher (iso-?) paraffins of low m. p.
Paraffin	Paraffins	Paraffins.

[fol. 832] From this table it will be seen that while the paraffins are conspicuous in American petroleum, shale products are remarkable for their richness in olefines. In consequence of this peculiarity of constitution, concentrated nitric and concentrated sulphuric acid act far more vigorously on shale products than on the parallel products from petroleum, and the proportion of paraffins given in the above table really represents the percentage by measure of hydrocarbons which withstand a consecutive treatment with nitric acid of 1.45 sp. gr. concentrated sulphuric acid, fuming sulphuric acid, and sodium hydroxide. Russian petroleum behaves with reagents much like American petroleum, but consists largely of cyclic hydrocarbons (naphthenes).

A much more satisfactory method, and one which gives fairly constant results, is based on the fact that paraffins and naphthenes do not react with bromine, while the hydrocarbons of most other series take it up freely, forming additive or substitution products (page 110).

The following table shows the results obtained by Allen as to *to* the action of bromine on various representative commercial products from shale, and American and Russian petroleum. The shale products were furnished by Mr. R. Tervet; those derived from American petroleum (with the exception of the gasolene and vaseline) were furnished by Mr. J. Merrill, of Boston, Mass.; and the Russian petroleum products by Messrs. Ragosine & Co. The solution of bromide in dry carbon disulphide was allowed to act on the dry oil for from 15 to 30 minutes in the dark, when potassium iodide was added and the liquid titrated with decinormal thiosulphate. After titration the solution was filtered, and the aqueous liquid titrated with standard alkali hydroxide and litmus. From the amount used, the proportion of hydrobromic acid formed was ascertained, and from this the bromine existing in that form was calculated.

From these results it will be seen that there is in every case a marked difference between the proportion of bromine assimilated by any of the shale products and the quantity which combines with the parallel product from American petroleum, especially in the lighter fractions. It is evident, however, that the results must not be interpreted too strictly, for an oil which was obtained by

"cracking" would be richer in olefines, and hence would show a higher bromine-absorption than one of another kind.

[fol. 833] The results yielded by the products from Russian petroleum are still more striking, though other samples of kerosene have shown higher absorptions (e. g., 15%) than those given in the table.

The following determinations by Mills and Snodgrass were made by the process described in Vol. 2, page 26.

Product	Sp. gr.	Bromine-absorption
Lubricating shale oil	0.860	22.2
Lubricating shale oil	0.870	20.6
Lubricating shale oil	0.890	12.6
Lubricating shale oil	0.900	11.7

Description of substance	Specific Gravity at 15.5°	Grames of Bromine reacting with 100 grm. of Sample	Bromine as HBr. per 100 grm. of Sample
Gasolenes—			
From shale	0.665	62.2	1.1
From American petroleum	0.650	17.9	3.1
Naphthas—			
Shale naphtha	0.720	67.2	4.0
C.naphtha from American petroleum.	0.706	18.3	.....
Burning Oils—			
From shale	0.813	51.3	3.0
From American petroleum	0.800	34.8	.....
From Russian petroleum	0.821	2.0	0.1
Intermediate Oils—			
From shale	0.850	48.2	.....
"Mineral Sperm Oil" (American petroleum)—	0.847	32.3	.....
"Pyronaphtha" (Russ. petr.)	0.868	1.9	0.1
Lubricating Oils—			
From shale	0.890	25.6	5.8
Cylinder oil (from shale)	0.890	11.0	.....
From American petroleum (heavy spindle oil)	0.900	11.7	.....
From Russian petroleum	0.904	4.9	0.8
"Champion Oil" (Amer. petr.)	0.911	9.9	0.8
Cylinder oil (Russian petr.)	0.909	5.8	0.6
Vaselines—			
From American petroleum (Chesebrough Co.)	0.856	11.3	1.8
From Russian petroleum		1.7	0.3
Paraffin Waxes—			
From shale (m. p. 52°)		1.7	0.5
From petroleum (m. p. 54°)		0.9	0.2

petroleum benzin be added to a mixture of 40 drops of sulphuric acid and 10 drops of nitric acid, in a test-tube, the [fol. 834] liquid warmed for about ten minutes, and then set aside for half an hour, or diluting it in a shallow dish

with water, it should not evolve the bitter almond like odom of nitrobenzene (difference from, and absence of, benzene).

The "petroleum benzin" of the German Pharmacopœia is the colourless, non-fluorescent portions of petroleum, having a sp. gr. of 0.640 to 0.670, and distilling almost entirely between 55° and 75°. On adding 2 c.c. of this liquid to a cold mixture of 1 c.c. of sulphuric acid and 4 c.c. of fuming nitric acid and shaking, no appreciable colour and no odour of bitter almonds should be produced.

The British Pharmacopœia (1898) defines "petroleum spirit" to be a derivative of petroleum, boiling between 50° and 60°, and with a sp. gr. between 0.670 to 0.700.

Petroleum spirit is liable to contain impurities, which unfit it for certain uses. If of good quality, it will leave no odour when evaporated on the hand, and when evaporated in a porcelain basin heated over boiling water, will leave no oily residue of heavy hydrocarbons. Boiled for a few minutes with alcohol and a few drops of ammonia, a brown colouration produced on subsequently adding silver nitrate solution indicates sulphur compounds, which render the sample unfit for use as a turpentine substitute, as it will be liable to discolour white paints. When petroleum spirit is agitated with warm water, the water after separation should be perfectly neutral in reaction, and should give no cloud with barium chloride (absence of sulphuric acid and sulphonates).

The sp. gr. is best determined by means of a hydrometer at 15° or if at another temperature, allowance is made according to the following table:

Sp. gr.	Correction for each degree
0.700 to 0.720	0.000820
0.720 to 0.740	0.000818
0.740 to 0.760	0.000800
0.760 to 0.780	0.000790
0.780 to 0.800	0.000780

Water cannot exist in notable quantity in petroleum spirit without rendering the liquid milky. If present to an extent sufficient to be thus visible, the liquid is rendered unfit for burning in sponge lamps, etc. The water may be removed by prolonged subsidence, or more rapidly and perfectly by agitating the sample with a little dry plaster of Paris.

[fol. 835]

	Petroleum spirit	Shale naphtha.	Coal-tar naphtha
Chemical composition. .	Contains at least 75% of paraffins, principally heptane, the remainder apparently olefines, with traces of aromatic hydrocarbons.	Contains at least 40 to 50% of olefines, principally heptene; the remainder paraffins. No trace of aromatic hydrocarbons.	Consists almost wholly of benzenes. A small percentage of open-chain hydrocarbons in some samples.
Sp. gr. at 15°	0.700	.0.718	0.876
Chiefly distils between.	65° and 100°	65° and 100°	80° and 120°
Solvent action on coal-tar pitch.	Very slight action; liquid but slightly coloured even after prolonged contact.	Behaves similarly to petroleum spirit.	Readily dissolves pitch, forming a deep brown solution.
Behaviour on shaking 3 volumes of the sample at 20° with 1 measure of fused crystals of absolute phenol.	No apparent solution; the liquids are not miscible, but set to a mass of crystals when cooled slightly beyow 0°.	The liquids form a homogenous mixture, often setting to a mass of crystals at 18° to 20°.	The liquids form a homogeneous mixture.
Reaction with bromine in the cold.	Combines with 10 to 20% of its weight of bromine.	Combines with upward of 60% of its weight of bromine.	Reacts slowly with a considerable proportion of bromine.

Benzin for Degreasing.—For this purpose it is desirable to choose one that does not contain a large percentage of very low boiling or a large amount of high boiling constituents. In the first case too much is lost by evapouration and in the second too much heating is required to expel all of the solvent from the fat, and the fat is also injured thereby. Most of the benzin should distil between 80° and 110°, 95° being considered the ideal mean.

Analyses of these oils consists in making distillation records with 100 c.c. of benzol in a suitable dephlegmator and noting the amount of distillate between each 10° intervals of temperature, starting at 70° and running to 110°. The rate of distillation is about 1 drop per second.

Shale naphtha, which is the lighter and more volatile portion of the oil obtained by the distillation of bituminous shale, is a product very similar to petroleum spirit in most of its properties and uses. Allen found, however, that the shale naphtha presents certain differences, which are due to a much larger proportion of olefines than exist in petroleum naphtha. The table on page 116 exhibits concisely [fol. 336] these differences, and compares the characters of a sample of coal tar naphtha with specimens of similar products from shale and American petroleum. Variation in minor details will be met with in different samples from similar sources. (See Crude Shale Oil, page 16.)

Mineral Burning Oil. Kerosene. Coal Oil

Under these names, and others more fanciful and less appropriate, are classed the fractions of petroleum and shale oil which are suited for burning with a wick. The petroleum product is often broadly described as "refined petroleum," and that from shale oil as "paraffin oil," but the latter name is often popularly applied to heavier oil from petroleum. The name "kerosene" is a contraction of keroselain, or "wax oil," and was origanlly a trademark adopted for a certain patented fraction of coal oil. The term has now been adopted as the most convenient to apply to mineral burning oils generally.

Kerosene is a colourless or yellowish oily liquid, often possessing a well-marked blue fluorescence. It has a characteristic taste and smell which it imparts to water, though practically insoluble in that liquid. It is only moderately soluble in alcohol, but is miscible in all proportions with ether, chloroform, benzene, petroleum spirit, volatile oil,

and fixed oils, with the exception of castor oil. It dissolves phosphorus, sulphur, iodine, camphor, many resins, waxes, fats, and softens india-rubber.

The commercial varieties of mineral burning oil are very numerous, and hence the physical characters are not very constant.

The sp. gr. of ordinary American kerosene is about 0.790 to 0.800, the parallel product from shale oil being 0.800, and from Russian (Baku) petroleum 0.822. Burning oils of higher densities are also largely manufactured, and are well adapted for special purposes.

The following are the characters and special applications of certain other varities of mineral burning oils:

[fol. 837] PETITIONER'S EXHIBIT No. 116

Petroleum, a Treatise on the Georgraphical Distribution and Geological Occurrence of Petroleum and Natural Gas; The Physical and Chemical Properties, Production, and Refining of Petroleum and Ozokerite; the Characters and Uses, Testing, Transport, and Storage of Petroleum Products; and the Legislative Enactments Relating Thereto; Together with a Description of the Shale Oil and Allied Industries.

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(Pages 431, 432, 437)

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has a specific gravity of 0.870 to 0.880 and contains most of the paraffin. On the other hand, where only small quantities

[fol. 838] of oil are treated, the still, B1, B2, may be dispensed with, the still, A, being connected directly with the coking stills.

In a continuous distillation process devised by Messrs. Young and Beilby[1] the still is of horizontal cylindrical form, and is partitioned transversely, a series of separate chambers being thus formed through which the oil successively passes. Each chamber is provided with a pipe leading to a condenser, and the furnace is so arranged that the heat is graduated, one end of the still being much hotter than the other. The oil enters the first chamber at the cool end of the still, and the residue is discharged from the last chamber at the hot end. This system has not hitherto been put into practical use.

The "once run" oil usually passes through three distinct stages of chemical treatment and distillation before it is marketable.

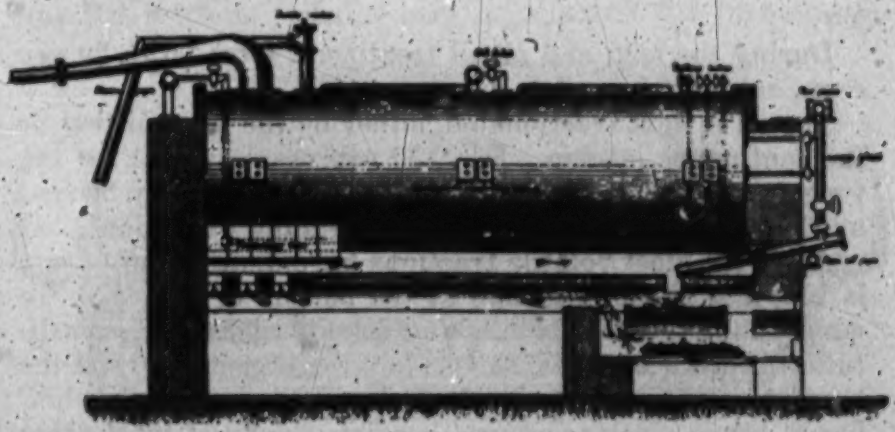


Fig. 180.

The agitators in which it is treated with acid and alkali, are of various forms, and vary in capacity from 2,000 to 20,000 gallons. They are set on different levels, so that, after the acid treatment, the oil may be run into a lower agitator for treatment with alkali. One form consists of a horizontal cylinder 6 to 8 feet in diameter, fitted with a shaft carrying paddles which revolve between fixed discs. Another form consists of a vertical cylindrical tank, 8 to 16 feet in diam-

[1] Patent No. 6,094, 1884.

eter, with egg-shaped bottom, in which the agitation is effected by means of compressed air.

The oil is treated at the lowest temperature which will prevent separation of solid paraffin—i. e., at about 100° F.—a temperature maintained by steam coils. The sulphuric [fol. 839] and used, may either be fresh acid of specific gravity 1·720, or may be the acid tar obtained as hereafter described in the treatment of another distillate. The acid is usually added in two or three portions, and admixture is effected by means of the air blast, the acid tar being separated after each addition.

After settling for at least four or five hours, the oil is run off by gravitation into the alkali agitator, where it is treated with soda lye of 1.3 specific gravity (60° TW.). The alkali may, like the acid, be advantageously added in successive quantities, the treatment commencing, in some cases, with the use of a little alkali of as low a specific gravity as 10° Tw.

During the acid and alkali treatment, from 26 to 30 per cent., calculated on the crude oil, is lost.

The oil is next fractionated, either by the intermittent or the continuous system. Fig. 150 represents a still for the former system. It is heated below as shown, partly by coal and partly by tar produced in the refining operations.

After the most volatile fractions have distilled off, steam is blown in through a pipe at the bottom of the still. In many cases, the distillate, with a density up to 0·770, constitutes the crude naphtha, and that up to a density of 0·850, the burning oil. The remainder of the distillate, which solidifies at common temperatures, consists chiefly of lubricating oils and paraffin. These three fractions are delivered from the condensers into separate tanks.

Although the crude-oil stills of Henderson may be applied for the continuous distillation of the once-run or other oils obtained in the process of refining, the inventor prefers another form of apparatus which he patented in 1883 (No. 540).

This arrangement (shown in Figs. 151 to 155) comprises a set of three horizontal cylindrical stills, each 7 feet in diameter and 19 feet in length, and each fitted with an outlet pipe in the bottom at one end. At the same end, but at a higher level, an inlet pipe passes into the other end of the still, so that the inlet and discharge are as far as possible apart.

The vapours from each still rise into the usual dome or vapour chest, 24, and pass thence into a "feed-heater," 26, where they raise the temperature of the oil as it enters the still. The oil circulates from still to still, as in the Henderson continuous system already described, and two or more residue stills, one of which is shown at 41, are provided to receive the residues from the third still, one being used while the other is being cleaned out.

[fol. 840] As coking takes place to some extent in the third still, this is fitted with plates or dishes, 42, with a view of promoting circulation of the oil, and preventing the adhesion of the coke to the bottom of the still, the carbonaceous deposit collecting on the plates, from which it is readily removed. These plates extend along the still, and the lower portion is formed with a curve, as shown, corresponding with that of the still. They are hinged to straps riveted to the sides of the still, and are supported by feet resting on the still bottom. Chains may be attached for turning up

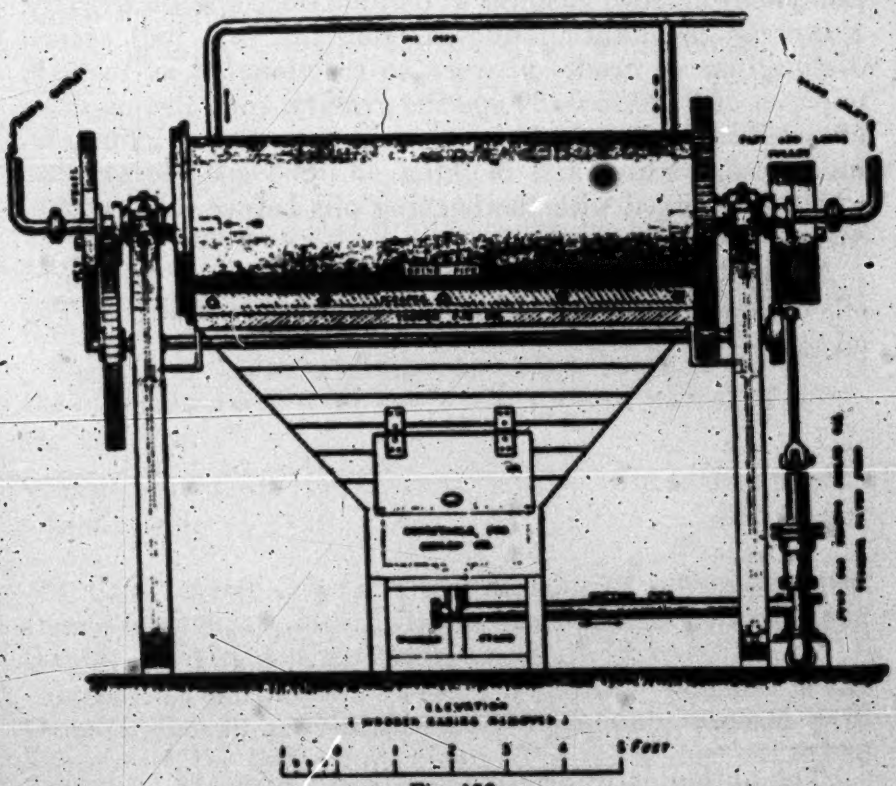


Fig. 156.

the plates for cleaning.[1] The oil circulates under the plates, up the sides of the still, and back towards the.

. . . . . .

Crude shale naphtha includes the crude "gasoline," of specific gravity 0·700 to 0·770, obtained from the shale distillation, and the light fractions from the first and second distilla- [fol. 841] tions of the crude oil. It is refined by agitation with 0·1 to 0·2 per cent. of sulphuric acid for fifteen minutes, followed by a similar treatment with 0·5 per cent. of acid. After settling for twelve hours, the tar is drawn off and the naphtha is run into another vessel, where it is agitated with 1 per cent. of caustic soda solution of 10° Tw., after which it is allowed to settle for twelve hours and is then distilled. The first distillate from crude gasoline (up to 0·695 specific gravity) is redistilled, the remainder (about 0·718 to 0·720 specific gravity) being classed as naphtha. The light portion yields finished gasoline of 0·640 to 0·660 specific gravity. Formerly the light distillates from the first and second distillations of crude oil were so fractionated as to yield naphtha of 0·720 to 0·730 specific gravity, for sale; naphtha of specific gravity of 0·750, for use in the refinery in dissolving paraffin scale; and naphtha of 0·800 specific gravity, which was mixed with the burning oils before third rectification.

At one time paraffin scale was produced from the heavy oils obtained in the first, second, and third distillations. The oil result-

. . . . . .

[1] The author is informed that these plates are no longer used.

[fol. 842] TRANSLATION OF PETITIONER'S EXHIBIT No. 117

French Republic, National Office of Industrial Property

Patent of Invention of February 5, 1903. XIV.—Chemical Arts. No. 329.076

5.—Essences, resins, waxes, rubber

Patent for Fifteen Years Applied for February 5, 1903, by Mr. Henri Vittenet (France). Process of Chemical Purification and Deodorizing of Petroleum Oils and Benzines and Similar Products. Patented May 18, 1903; Published July 25, 1903

This invention has for its object a process of chemical purification and deodorizing of petroleum oils and benzines and, in general, of all similar products.

This purification and deodorization are obtained in the following manner:

One agitates strongly, for a quarter of an hour, a mixture of:

"Petrole"	100 liters (10 parts by volume)
Sulphuric acid of 60° Be.	10 Kilogr. (1 part by weight)

One permits it to rest until decantation (about a quarter of an hour); one decants the oil and shakes it strongly for some minutes with 10 kilograms (1 part by weight) of liquid bisulphite of soda (an aqueous solution of 36° Be).

One leaves them in contact for some hours, one decants the oil again and shakes it several minutes with the following mixture:

Water	100 liters.
Caustic soda	400 grams.

[fol. 843] After this agitation, all odor of sulphurous acid should have disappeared. In the contrary case, a little soda is added and shaken up again.

It is then permitted to rest. When the emulsion is destroyed, the oil is decanted and thoroughly washed with water until the latter runs clear. The oil is then caused to pass into a well dried receptacle and is digested with occasional shaking with anhydrous calcium chloride or with calcium carbide until it has acquired a perfect clearness.

According to the degree of purification which is desired to attain, the product, once purified, may, after the first treatment, be subjected to a second identical treatment.

Finally, by way of a variation, these two successive treatments can be replaced by a single one on condition of substituting for the agitation with sulphuric acid alone, an agitation for ten minute*d* with the following mixture:

Sulphuric acid of 66° Beaume	10 kilograms (1 part)
Potassium bichromate	10 grams (0.001 part)

for each 100 liters of petrol (10 parts), the rest of the treatment being the same.

The proportion of potassium bichromate that is added to the sulphuric acid can be varied a little, following the degree of deodorization that it is desired to attain.

To sum up, the inventor claims as his exclusive property:

First, the process of purifying crude petroleums for the purpose of removing their disagreeable odor, substantially as described.

Second, The Application of this process to all other products than petroleum, with the object of arriving at the same ends.

Third, The application industrially of these petroleums and other products purified by the indicated process.

Lyons, February 5, 1903.

J. Germain, by Mr. Henri Vittenet, Attorney.

[fol. 844] TRANSLATION OF PETITIONER'S EXHIBIT No. 118

Sammlung Chemischer und Chemisch-technischer Vortaege

Vol. 5, 1900, pp. 189-204 and 212-229

Destructive Distillation in the Mineral Oil Industry.

By S. Aisinman, Technical Director

(With 23 illustrations)

First Part

The development of the mineral oil industry with regard to the working of mineral oils into various marketable prod-

ucts offers a rather peculiar situation. At some times we note that one product seems destines to play a predominnating part, and then again at others it is another product, according to the situation of the world's markets the requirements of which closely guiding production is almost entirely governed by the world market.

[fol. 845] This occurs so much more easily since petroleum, as to its chemical nature, is no homogeneous body possessing fixedly established unalterable properties, but rather a mixture of closely related hydrocarbons. The different members of the long series of hydrocarbons differ from one another primarily by the successive increase of the carbon in the molecule as well as by the way and manner of linking between the carbon and the hydrogen in the construction of the chemical cell.

However, hand in hand with the divergence in molecular composition we note also a change in the physical properties which manifests itself in higher specific weight, boiling point, flash point, higher viscosity, as well as state of aggregation. Also the color of the different hydrocarbons is connected therewith, and comprises an entire scale ranging all the way from absolute whiteness resembling water through all the shadings of yellow, red, green, and blue up to the deepest brown and black.

These properties together with the extreme ease of solubility of the different hydrocarbons when mixed with one another constitute the basis of petroleum working.

By taking into consideration the boiling temperature of the different members of petroleum, it is possible to isolate individual groups—educts—from the mixture, and to thus form new bodies exhibiting wholly different chemical and physical properties. By mixing the different bodies in any desired proportions, the series of possible final products can be extended well nigh ad infinitum.

Still, in the course of the time, fixed types have been worked out which with due consideration of the physical nature of the different products as well as of the purpose, as benzin, kerosene, lubricating oil, asphaltum, and coke present certain characteristic features.

From among the products above enumerated, petroleum proper or kerosene was destined from the very outset in the development of the mineral oil industry to play a leading role, indeed, as it were, it constituted the raison d'etre of the new industry which originated in the second half of this

century. This becomes so much more easily understood if we keep in mind the situation in the illumination art of those days, and the high cultural progress embodied in the opening up and introduction of a new illuminating source.

The main problem in the working of mineral oil as well as the path and direction to be followed were closely outlined, [fol. 846] i. e., to realize as high as possible a yield in illuminating oil from the mineral oil. However, not all of the ingredients in mineral oil were suited for this purpose. The easily volatile products flashing at a low temperature, i. e., the benzins, could be added to or be contained in the illuminating oil only in small quantities, as otherwise there was a risk of endangering the confidence in *in* and safety of the new illuminant, while the use of the heavier oil components was rendered impossible because of their slow rise (capillary action) in the wick, incomplete combustion owing to insufficient access of air as well as the unsatisfactory influence upon the uniform course of the burning of the petroleum or kerosene in the lamp.

The residues of crude oil constituted a ballast, as it were, for mineral oil producers, since the energy hidden in them (and which were later used for lubricating purposes in mechanical engineering and traffic) had not yet been appreciated at that time.

It was, therefore, a great step forward in the field of mineral oil manufacture when just by accident it was discovered that the residue could be worked so as to exact illuminating oils therefrom.

On this phase of the matter, let us see what Leet says in his book entitled "Petro leum Distillation":

One cold afternoon in the winter of 1861, the contents of a wrought-iron upright distilling apparatus in a petroleum refinery in the State of New Jersey had been driven off to about one-half. The distillate had already reached a spec. gr. of 0.809, and showed marked evidence of dark coloration. The distiller, therefore, had the intention to run the distillate into the receiver for heavy oil about one half hour later.

After he had started a rather strong fire under the boiler in order that the distillation may be kept in good running order for a time, he left the works with the intention to return soon. However, he was delayed and came back only after four hours. How great was his surprise and consternation when he noticed that from the boiler only a thin jet of

oil quite cold, light in color, and of a spec. gr. of 0.786 was flowing into the receiver.

As he was unable to explain this phenomenon which was entirely conflicting with his previous experience, he turned off the distillation entirely, and waited for the arrival of the owner of the works. When the latter came, only a very thin jet of oil could be seen flowing at the end of the cooling coil, [fol. 847] the spec. gr. of the latter having meanwhile decreased to 0.769.

The owner was a chemist, and he, therefore, arrived at logical inference by considering cause and effect that the decrease in temperature under the boiler had been causative of the lower spec. gr. of the oil vapors, and that, by continuing the process, a higher yield in illuminating oils could be obtained.

Now, in order to study the processes taking place inside the boiler, he constructed a large glass retort, and it was then found that after distilling off the main fraction of the mineral oil (the petroleum or kerosene) as far as spec. gr. of 0.804 by the subsequent reduction of heat supply, lighter distilling vapors started to be produced from the mineral-oil residues.

The oil was incidentally volatized and re-condensed, it rose and fell, being re-distilled possibly thousands of times before the light oil vapors eventually left the retort. The observations which were then made in large-scale manufacturing tests, demonstrated that in the same measure as the spec. gr. of the final products became lower, the oils turned darker in color, and this seemed to point to undue dissociation.

Since the original method of building the still into masonry had been developed to a point where during heating both sides of the boiler as well as the bottom thereof were heated, the attempt was made to obtain lighter distillates by building masonry around the still, in this manner that either the bottom alone or else both the bottom and the walls of the still could be heated at will.

Now, the upper third of the boiler including the cover or roof was lined with concrete, the central portions surrounded by brick work, while only the lower third of a height of about 18 inches from the grate beam was exposed to direct fire.

The smoke flue which surrounded the side walls of the boiler, was furnished with a damper so that the heating gases, after heating the bottom, could be led directly to the smoke stack.

Now, the result of this masonry construction was more than satisfactory. When changing the direction of flow of the heating gasses and by reducing at the proper time the intensity of the heat, a yield in illuminating oil about 20% higher was realized. The color of the distillates thus obtained was light, and the latter has a spec. gr. of 0.800. The length of the distillation process was hardly greater in [fol. 848] the new method than before, and hardly any more fuel was consumed, and yet by far smaller quantities of heavy oils were obtained, indeed, only 5% of the total yield.

The new process did not remain a secret for a long time, indeed, after a short while it found its way into the refineries of Jersey City, Brooklyn, Greenpoint, and of Oil Creek."

I. Earlier Types of Cracking Plant

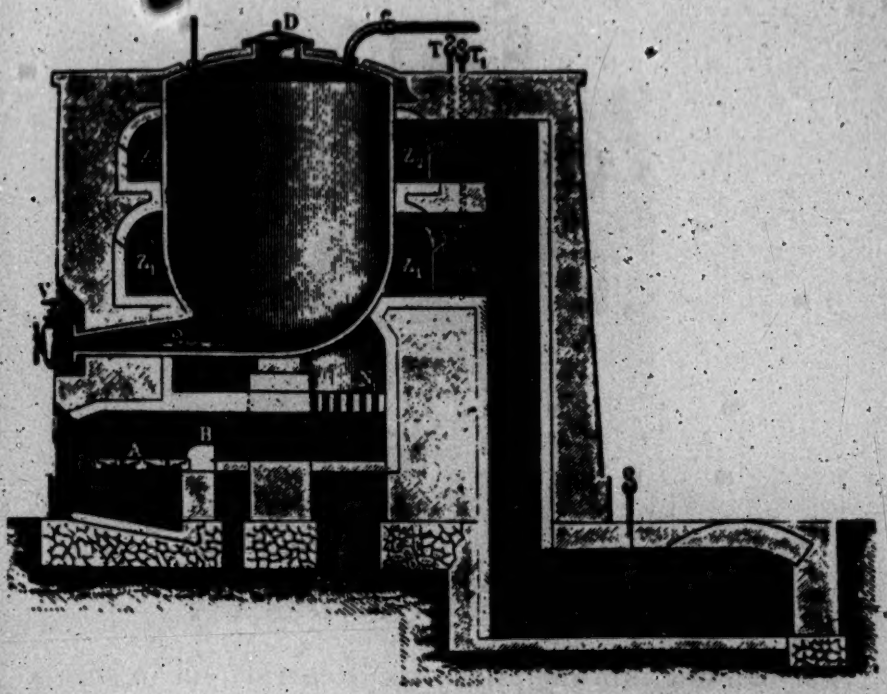
With progressing perfection of the manufacturing methods, the destructive or cracking distillation so-called became soon a separate branch of the works. The residues were then no longer worked in the crude oil still, but rather in a special plant adapted to this particular purpose.

The distilling apparatus used in this connection were first constructed entirely of cast iron, later of a combination of cast and wrought iron. However, after Martin steel had been found to be a material very resistant to heat, the boilers were made entirely of wrought iron. Such boilers even under heavy duty conditions are able to withstand operations for several years; but then the bottom and sometimes also the shell rim must be replaced.

The advantages of this material compared with cast iron consist in lower cost, saving in fuel, and greater capacity of boilers, which in the case of cast iron would lead to abnormally large wall thickness. Another point is that with wrought-iron boilers no such accident as cracking of the wall due to imperfect cast material during the first operation is liable to happen, whereby the boiler often is ren-

dered entirely unserviceable. These viewpoints have also led to an abandonment of the scheme of combining a wrought-iron shell with a cast-iron bottom.

Fig. 1.

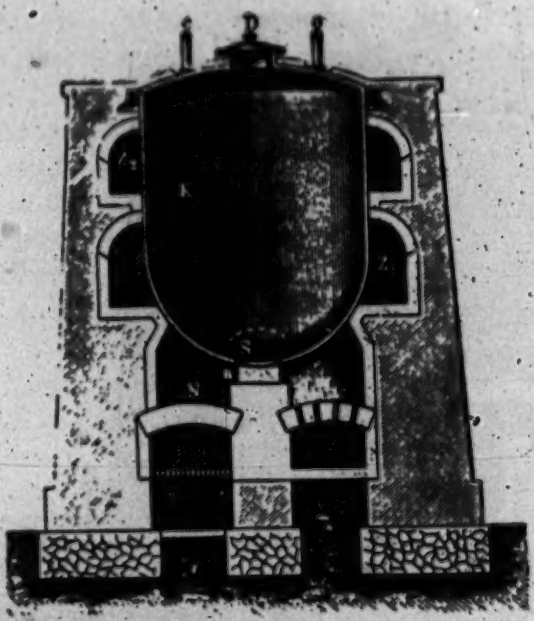


[fol. 849] In Figs. 1 and 2 the construction of a cast-iron distilling apparatus is shown together with the mode of building the brick-work. The shell of the boiler is cylindrical, the bottom bowl-shaped.

The latter by means of an appenadge part is rested upon the masonry, and is provided with a drain pipe S in case the cracking operation is to be conducted only as far as an asphaltum-like residue. The wall thickness of the boiler ranges from 25-30 for the upper edge of the boiler and 40-50 mm. at the bottom. The diameter of the boiler is from 1500 to 2000 mm., height 1000 to 1500 mm. The capcity is usually sufficient for from 40 to 50 metric hundredweights of oil, the requisite rising space being taken into consideration. The boiler top made of cast- or wrought-iron is connected with the shell by screws or rivets to insure tight joints, and is provided with pipe ends for

oil and vapor of from two to three inch diameter, a manhole (D) of 500-600 mm. diameter and two overflow tubes 3-4 inch inside diameter (*c*, *c*).

Fig. 2.



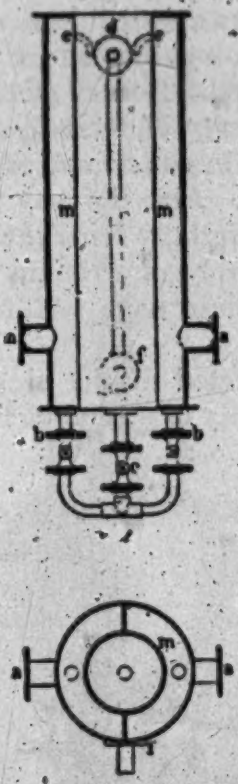
The building into the brickwork is carried out in such a way that the gases reach the space underneath of arch N from the furnace A by way of the fire bridge B, thereby heating the bottom of the boiler. The net-shaped arch protects the bottom from tongues of flames. From there the gases reach the sides of the boiler laterally through the flue Z_1, 500 mm. wide and 600 mm. high. With the damper T_1 being closed, the gases must flow through the flue Z_2 and are made to overheat the boiler walls also in the upper third of the shell, whereupon, with damper T closed they are conducted to the chimney.

If the boiler is to be heated only at the bottom and the lower third of the shell, the damper T_1 is opened, while damper T_2 remains closed.

To enlarge the rising space (free space above liquid), and in order to return heavy vapors that have been carried off and submit these to renewed dissociation, the boilers are furnished with dephlegmators. A device of this kind is il-

lustrated in Fig. 3. The same consists of a double-walled wrought-iron drum 500-600 mm. diameter and about 1500 mm. height.
[fol. 850]

Fig. 3.



The mixture of heavy and light oil vapors reaches the dephlegmator by way of laterally disposed admission pipes of about 3″ diam. about 500 mm. from the bottom of the drum and are separated by external air cooling with incidental condensation of the heavy vapors. The condensate flows through the pipes *b* and *e* provided at the bottom of the dephlegmator back into the boiler, whereas the light oil vapors enter at *c* into the inner space of the dephlegmator reaching from there the cooler by way of a 4-inch overflow pipe at D.

The cracking equipment provided with dephlegmator is shown in Figs. 4 and 5. In this case recourse is had to the combination of wrought-iron shell and cast-iron bottom. In order to avoid leaks, the shell is not flange-connected

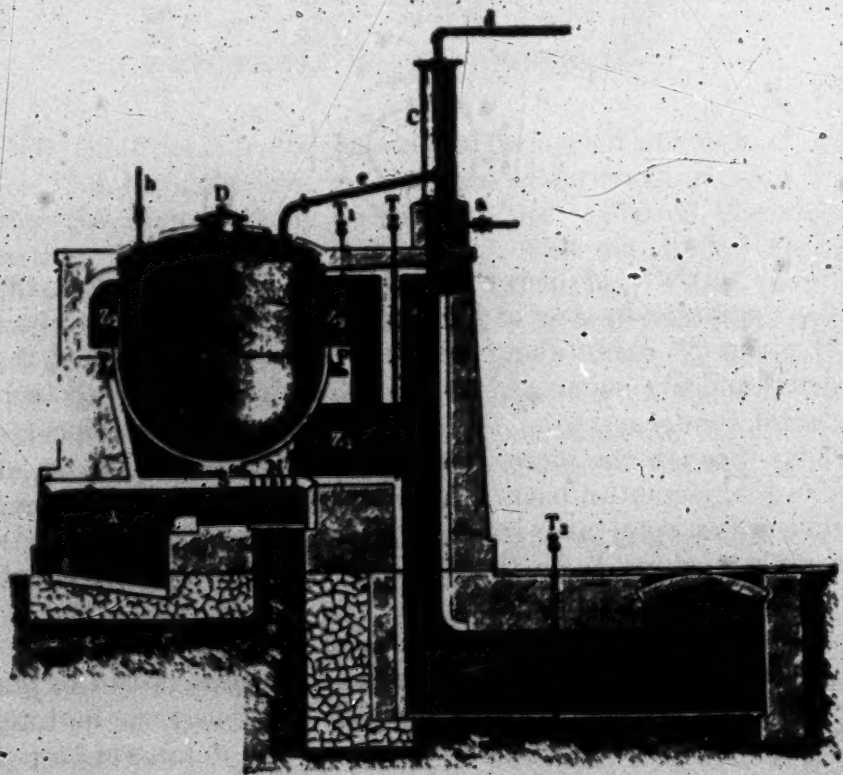
with the bottom, but is shifted into the bottom, being riveted together with the bottom by the aid of a wrought-iron packing or caulking piece.

In order to diminish stresses and tensions in the cast material the boiler is rested upon feet or claws P. The wrought-iron shell has a wall thickness ranging between 12 and 15 mm., the cast-iron bottom has a thickness ranging between 60 and 70 mm. Boilers of this type have already been built for a capacity of from 60 to 80 metric hundredweights. The cover has the same fittings as in the boiler previously described. Also the way the brickwork is built does not differ substantially from the first plant. A cracking boiler made entirely of wrought iron of the kind frequently used even these days is illustrated in Figs. 6, 7 and 8.

The boiler constructed of the highest grade of Martin steel consists ordinarily of a shell of 15 mm., of two borders

[fol. 851]

Fig. 4.



riveted and calked in double rows and a 20-mm. flanged bottom made in one piece, the joint being made oil-tight. Shell and bottom are snugly united by double riveting. The diameter of the boiler varies between 2500 and 3000 mm., the height ranges between 2000 and 3000 mm. The arched roof made of 10-mm. plate has a filling pipe piece of about 100 mm. inside diameter, two smaller pipe pieces of about 50 mm. inside diameter for steam and air, a manhole of about 600 mm. diameter, and a dome of about 600 mm. diameter and about 500 mm. height with a waste pipe of a

[fol. 852]

Fig. 3.

diameter between 100 and 150 mm. If a dephlegmator is provided in lieu of the dome, then the boiler is furnished with two laterally disposed pipe pieces of 100 mm. inside diameter for the overflow pipes.

The brickwork is carried out in the following manner: An extension furnace serves for the burning of coal, or of liquid or gaseous fuel. This furnace is lined internally with refractory material, and contains the heating room or furnace proper. In this manner the flame is not produced directly underneath the boiler bottom. It is disposed somewhat on the side and connects with the pillar made of refractory material, which, disposed in the middle of the boiler, serves both as a support for the boiler as well as for carrying the netlike arch. The row of rivets which joins the bottom and the shell is protected against the direct action of the intense heat by refractory material. A flue of about 500 mm. width and 600 mm. height surrounds the lower part of the boiler, while the rest of the boiler is enclosed by solid masonry. The arrangement of the dampers allows of conducting the heating gases directly to the chimney instead of by way of the lateral flues.

Other parts of the cracking equipment are a cooler (condenser), a distillate distributor or separator, the pipe connections, and the receivers for the different kinds of oil.

The cooler or condenser consists mostly of a cast- or wrought-iron coil pipe which is built into a square vessel. The mouth of the coil corresponds to the inside diameter of the overflow pipe of the distilling apparatus, and it gradually tapers towards the outlet to an inside diameter from 80 to 50 mm. Before the coil comes out of the cooler vessel, there is inserted therein a pipe of about 50 mm. diameter which protrudes beyond the cooling vessel, and which is used for the purpose of carrying off the permanent gases. It is only in extremely rare cases that the gases are allowed to escape into the atmosphere, for in the majority of cases they are conducted to a gasometer (gas container) in order to be used for illuminating purposes after convenient purification, or else they are fired under the boiler. The cooling is based upon the counter-current principle, the oil vapors entering the coil at the top end thereof, while the cooling water is supplied to the vessel at the bottom end, the heated water being conveyed away through an overflow at the top.

The length of the cooling coil as well as the diameter of the same are chosen in accordance with the hourly output of the boiler.

After the oil vapors have been condenser in the cooler, they are admitted to the distributor or separator so-called. The same consists either of a wrought-iron vessel which is separated by partitions into several compartments for the various kinds of oil, and is connected with the different receivers by cocks and piping, or else it consists of a closed wrought-iron container of about 500 mm. width and depth and about 600 mm. height. This container is connected with the cooling coil through a siphon, and terminates through a system of cocks and pipes in the different receivers.

[fol. 853]

Fig. 6.

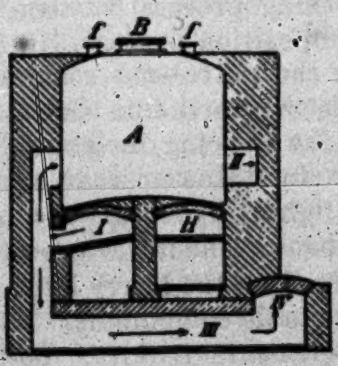


Fig. 7.

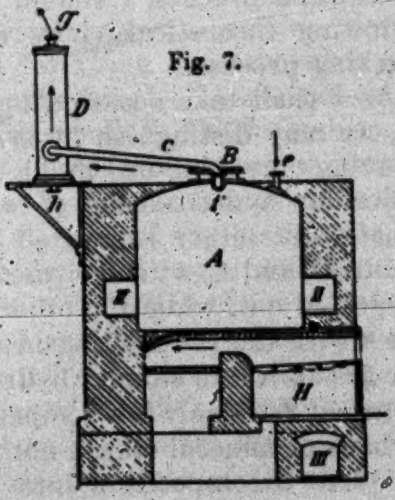
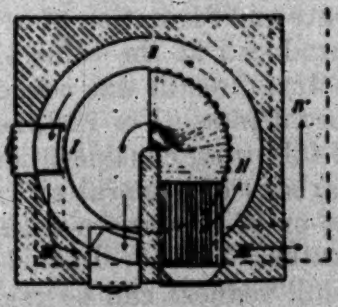


Fig. 8.



At the front end of the separator there is a tightly closing iron door which allows of the taking of samples as well as

of the observation of the distillation process. By turning the cocks, the condensate is conducted either into the one or into the other receiver. The second kind of distributor has the advantage of greater safety since in this case a fire can be fought much more easily in the open vessel not to mention the fact that the latter contains larger quantities of oil.

The receivers finally are closed square or round reservoirs or receptacles of wrought iron adapted to receive from 100 to 200 hectoliters. They are provided with inlet pipes, a manhole (mostly with water seal), a measuring [fol. 854] gauge tube, a drain pipe with fittings, and a steam coil, in order that the contents which are liable to clog can be liquified again.

Before I come to explain the manner of conducting the distillation process, I should like to draw attention to the following theoretical views regarding the nature of the cracking process.

As I shall take occasion to explain in more detail later on, we may distinguish in the cracking process between a cleaving (breaking-up) and a decomposition process. High-molecular hydrocarbons of which the petroleum residues consist are either separated or decomposed into the elements H and C with one part of the C being incidentally separated out, while the other part in status nascene combines with the H resulting in new lighter hydrocarbons, or else are split into simpler hydrocarbons. The latter process occurs at relatively low temperature since the heavy hydrocarbons of mineral oil are not very stable compounds. The complete decomposition into the elements requires, however, temperatures of red glow. But under these conditions, rearrangements and formation of aromatic hydrocarbons are readily produced at the same time. In analogy with organic chemistry, the still was conceived in the sense of a large incandescent pipe. For instance, in Veith (Das Erdol), we find the following considerations: "The decomposition of hydrocarbons of mineral oil is based upon the contact of the same or of its vapors with the hot walls of the distilling apparatus. * * * In this sense, the cracking boiler kept at dull redness can be regarded as a large pipe where the heavy oils undergo decomposition by contact thus resulting in a large percentage of aromatic hydrocarbons.

We further take from his explanations "that the relation between the lighter hydrocarbons due to decomposition and the heavier hydrocarbons is rather constant; and the more specifically lighter hydrocarbons are produced, the more specifically heavier hydrocarbons are obtained."

Thus, according to Veith, the apparatus should be so built and arranged that the heavy fractions and their vapors should be brought in contact with the overheated surfaces for as long a time as possible. The hotter the boiler walls, the speedier the decomposition, and the more light and correspondingly the more heavy portions are formed. Although the mode of decomposition which the heavier oils undergo in this operation has not yet been fully explained, it can nevertheless be assumed that they [fol. 855] are due to dissociation and subsequent polymerization.

This conception is characteristic for the earlier plants where, as a matter of fact, a far-going decomposition occurs, a fact that is sufficiently proved also by considerable deposition of coke in the cracking boilers, the formation of considerable amounts of heavy condensable gases (methane, ethane, ethylene, etc.) as well as the production of markedly aromatic compounds towards the end of the distillation.

Strange to say, the original idea which regarded the real value of the cracking process in a reduction of the temperature, has been left unobserved and has been fully appreciated and considered only in more recent installations.

Now, as regards the running of the distallation process proper, the same depends not only upon the nature of the plant, but in part also upon the property of the material to be worked.

The initial stage of the distillation process consists in boiling out the oil, in other words, in the complete dehydration of the oil. This stage must be carried out with great care in order that foaming and boiling over the boiler content on account of unduly rapid production of steam may be prevented. With decreasing water content, a distinctly perceivable boiling of the oil becomes noticeable which appears only upon the disappearance of the last traces of the water. The fire is made stronger until the boiler starts to run, that is to say, until a jet of oil is seen in the separator. During the interval between boiling out stage and starting of run, care must be taken to ascertain whether no

pressure exists in the boiler, a situation apt to arise in case of clogging of the cooler coil by the last distillation products. The first runnings are collected separately since they are ordinarily mixed with the heavy dark oils that had remained in the condenser oil, and since they have a disagreeable odor and unsightly color. After the distillation has really started, a uniform jet of light oil flows out of the condenser. By careful control of the fire, care should be taken to keep the distillation at as constant a stage as possible and to allow of variations of the distillate only inside definite limits of spec. gr. ordinarily between 0.800 and 0.830. By an unduly rapid increase in temperature only the contrary of what is expected would be obtained, that is, a heavy distillate of dark color. Hence, the process is conducted very slowly. In this manner, also the heavier [fol. 856] products that have been carried off are given a chance to return to the boiler, and to undergo renewed breaking-up.

Before about 50% of the heavy oil in the petroleum have been decomposed, several days usually elapse. The smaller the content of the boiler becomes the harder it is to regulate the decomposition, since the brickwork usually has stored up a great amount of heat, not to speak of the fact that profuse separation of coke at the bottom and the walls of the boiler constitute a layer of low heat conductivity. Hence, in this stage of the distillation heavy oils are obtained, and these are rich in pyrogenous paraffin.

According to spec. gr., viscosity, and color the heavy oils are separated into blue and green oils. They constitute about 15 to 20% of the total yield of distillate.

Towards the end of the distillation, the products obtained are gradually heavier and solidify at ordinary temperature; hence, these hardly deserve the term oil, and they are very rich in aromatic hydrocarbons. Upon the arising of these products dry steam is admitted into the boiler, the return of heavy oils from the dephlegmator is shut off, and the distributor or separator is choked. The steam carries off the last products from the boiler, and conveys the same mostly into a separate chamber (instead of by way of the separator), where the hydrocarbons become deposited in the shape of fine yellow dust. In order to free the coke from the last traces of oil, a rather intense fire is kept up under the boiler while the steam is passed through. It is

only put out after the steam shows clear characteristics of condensed wate*d*.

By the heat accumulated in the boiler some more heavy brownish-yellow gases are produced, and these are expelled from the boiler only by the renewed and continued chasing of steam through the boiler.

During the last distilling stage the water admission to the boiler is shut off, in order that stoppering of the cooling coil by easily solidifying oil may be prevented. The condensates running off, on the contrary, are properly to be kept at a temperature of from 40 to 50° C. About 6 hours after termination of the distillation process the manhole of the boiler is opened, and inside another 24 hours, after thorough cooling, the coke is removed from the bottom and the walls. The yield amounts to

[fol. 857] Illuminating oil	about 60%
Heavy Oils	" 20%
Coke	" 10%
Gases and losses	" 10%
	100%

The illuminating oils obtained by decomposition distinguish themselves by ready oxidizability, and for their chemical purification and refining they require a higher percentage of high-grade sulfuric acid. The refining losses are rather high since the hydrocarbons react intensively with the sulfuric acid. By means of pure 66-degr. sulfuric acid alone it is not possible to produce water-light or slightly yellowish petroleum. But more success is achieved by the use of cleum of about 10%.

The refining process, therefore, is carried out in the following manner. The distillate is first treated with about 0.3% soda lye of from 3 to 4 Be., thereupon it is washed with water, and the last traces of water are eliminated by about 0.5% 66-degr. sulfuric acid. The oil thus dehydrated is then asitated by air with 10-degr. cleum used in quantities of from 3 to 4% for about one hour. A still better plan is to use the Wolf apparatus and treat the oil with the acid (admitted through nozzles), this being followed by washing with about 2% 66-degr. surfuric acid after draining the sulfo-products that have been separated.

The acidulated oil rid of acids and tar is thereupon freed from whatever free sulfuric acid may still be contained therein by washing with water and neutralization with soda lye of from 3 to 4° Be used in quantities ranging between 0.2 and 0.3%. By renewed washings with water followed by filtration through salt or sawdust, the petroleum (kerosene) is made ready for consumption. Now, this product usually has a spec. gr. of from 800 to 820, and its hue lies around 80-90 mm. Stammer. In order to get a flash-test between 20 and 21° C. (Abel tester) the distillate prior to refining is freed from the more volatile components by blowing steam therethrough.

Although this Petroleum has all the outside marks of a marketable product, it is seldom sold in pure state, on the contray, usual practice is to mix it with the kerosene obtained from crude oil. The blue oils coming over after the illuminating oils have a spec. gr. of 0.800 to 0.900, a viscosity ranging between 2 and 4 at 20° C. in the Engler viscosimeter, and a solidification point of about 5 to 0°, according [fol. 858] to the origin of the crude oil residues. The fresh distillate has a light-yellow color which when exposed to the air, turns very soon into an intensive blue to oxidation by the air. This product is used either in the form of what is known as gas oil for the production of oil gas, or else it constitutes the starting material for carriage grease manufacture.

The very heavy products have a spec. gr. of from 0.905 and 0.930, and a viscosity of from 6 to 10, at 20° C. in the Engler meter. On account of their very high paraffin content they often solidfy even at ordinary temperature. Their color is a distinct green. They are used for the manufacture of carriage grease, or else, and this is probably mostly true, they are mixed with the blue oils above referred to for paraffin extraction. The oils liberated from paraffin are then worked for light lubricating oils.

The coke has a steel-grey color, is very porous and light, and is mainly used for the manufacture of carbon electrodes, but also for the manufacture of calcium carbide.

In order to spare the distilling boiler, manufacture is often adjusted to the production of heavy tar instead of to coke, the tar then serving for fuel.

Looked at from an economical viewpoint, the earlier cracking installations offer but little practical advantages.

Apart from the fact that for the products obtained fair prices are not obtainable, the fuel consumption for producing the material is rather high, and the burdens of amortization of plant rather heavy.

Also the production based on high kerosene yields from the crude oil by working the residues has lost most of its importance and value. The gradual opening up of powerful mineral oil deposits had a depressing effect on the prices for the raw material and makes the decomposition of crude oil residues a less remunerative proposition.

On account of their high thermal value, mineral oil residues, by the way, find an increasingly larger market as fuel for locomotives, steamers, and industrial works. Russia and America are hardly in a position any longer to satisfy the demand for liquid fuel, and they more and more reduce the production of petroleum so-called (kerosene) in order to have at disposal only a relatively large quantity of residues. Especially in Russia, the decrease in production per annum of petroleum is decreasing all the time compared with the volumes of mineral oil mined. The yield [fol. 859] has gradually decreased from 50% to about 25%, and it seems that in the near future these figures may be as low as 10 to 15%.

It is only in countries with a less developed crude oil industry, such as Austria, and Rumania, where the use of liquid fuel is still in its infancy, the cracking distillation is flourishing. But also, in these parts of the world, the older and more costly processes are gradually being given up, and better and more efficient apparatus of the kind to be described in the next chapter are employed.

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Destructive Distillation in the Mineral Oil Industry

By S. Aisinman, technical director

Second Part

III. Bagosin's Destructive Distillation Process

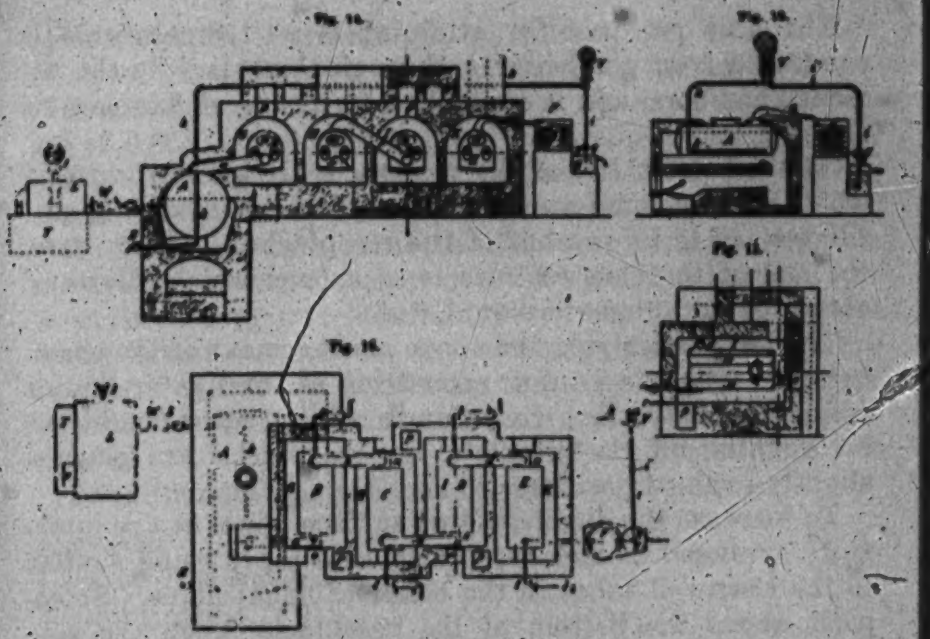
The distillation method patented in 1897 and adapted to the working of residual materials of mineral oils to obtain

kerosene and ozokerite, insofar as its fundamental ideas are concerned, remind one of the Aleksejeff apparatus and method demonstrated 10 years ago during the Petersburg Naphtha Industry Exhibition. The novelty of the Aleksejeff method resided in the introduction of light hydrocarbons or the so-called parmanent distillation gases (in lieu of the super-heated steam) for the purpose of producing the distillation; further in the superheating of the oil vapors in special receptacles for the object of splitting and breaking up the heavy oil vapors into kerosene-like hydrocarbons.

Now, since the Ragosin method can be regarded as a refined and elaborated form of the Aleksejeff method we believe the latter derserved to be described more fully in this place. As alr-ady pointed out, distillation in this process is accomplished by the aid of benzin vapors in lieu of superheated steam. For this purpose there are employed both [fol. 860] the difficulty condensable gases formed during the distillation as well as light hydrocarbons especially collected in a vessel for this very purpose. The light hydrocarbons which form during the distillation reach the condenser conjointly with the readily condensable distillates; they are then separated from the distillate, and pumped back into the boiler. This method of distillation was first applied in continuously as well as in intermittently operating apparatus.

Fig. 13 shows the construction of an intermittently working distilling boiler A from which the light hydrocarbons together with the distillates are conveyed through pipe *a* into the condenser F. At the bottom end of the cooling coil *s* is a three-way cock *g* whence a pipe *h* is led to the receptacle R, the end thereof dipping 2 or 3 inches into the liquid.

Now, this pipe conducts the condensate from the condenser L. Another pipe goes to the gas pump (exhauster) which forces the light difficulty condensable hydrocarbons back into the boiler A through the pipe K. Pipe *k* reaches almost as far as the bottom of the boiler, and it is provided with small holes through which the gases of the distilled liquid are allowed to pass.



Upon a similar principle is based the apparatus illustrated in Figs. 14, 15 and 16, adapted to continuous operation. From the boiler A the distillation vapors mixed with light hydrocarbons reach the first receptacle B by way of the pipe *a;* the portion that fails to be condensed here is passed on to the second receptacle C by way of pipe *b* and from there in gradually smaller quantities through *c* to D, next through *d* to E, being finally run through pipe *e* into the chilling coil *s* of condenser F. Similarly as shown in Fig. 13, a three-way cock is provided at the bottom end of the cooling coil whereby the light products are conducted to the pump, and the condensate to the receptacle.

Receptacles B, C, D and E are contained in brickwork chambers G, H, J and K. Both the chambers as well as the receptacles are kept at different temperatures, according to the products to be obtained therein. The closer the receptacle is to the boiler, the higher will be its temperature. For instance, the temperature of the first receptacle ranges between 360 and 400° C. and furnishes vaselin (probably protoparaffin), the second receptacle C has a temperature between 250 and 300° C and contains engine oils; C at a temperature between 150 and 200° gives solar oil, whereas [fol. 861] in D, at 80 to 100° C, kerosene is retained. Hence, it is only the benzine that reach the condenser.

The heat required for attaining these temperatures is conducted from the boiler A through chan-els P to the various chambers, and is controlled by means of dampers or slides, *r*, *r*."

At the bottom end of the receptacle are blow-off cocks 1 which are in communication with condensers in case the distillates are to be run out of the receptacles. At any rate, the end of the blow-off cock is at a level which allows of obtaining an automatic liquid seal.

The idea underlying the above arrangement of the chambers is to allow a readier separation of the lighter liquids from the heavy oils. In order to attain better conditions for running off the distillate, the receptacles are given a slightly inclined position.

To increase the dephlegmator surface, pipes *m* are internally arranged in each receptacle, said pipes being similar to the Cornwall tubes in the boiler of 4qual name. Somewhat above the bottom of the receptacle, upon the side opposite the drain tube 1, there are connecting pipes *n* for the overflow pipes *b*, *c* and *d*. They are furthermore furnished with manholes for cleaning the receptacle.

Boiler A is continuously supplied with the liquid to be distilled coming from tank *s*, whereas this tank is supplied in turn from a second tank T located at a lower level. Pump *t* which is inserted provides the tank L with more raw material than is required for the boiler, the excess in quantity being returned into the lower container by way of overflow *u*, the latter being arranged in such a manner that the level of the liquid in still A remains constant in spite of the pressure.

In order to avoid undesirable heating of the raw material contained in tank L by the tube *a*, the same is enclosed in a cooler W. The cock Z serves for emptying the boiler. If in the boiler mineral oil residues are worked instead of crude oil, the number of receptacles can be reduced to two. Although the quantity of light hydrocarbons non-condensable in the cooler depends upon the intensity of the cooling, there is as a rule obtained an excess which through pipe *i'* can be conveyed away and be used for some other purpose.

In the experimental work conducted on a rather large scale with the Aleksejeff apparatus in the Zollikofer refin-

eries (near St. Petersburg), an illuminating oil distillate of spec. gr. 0.824 was obtained from the mineral-oil res- [fol. 862] idues. After redistillation the same has a spec. gr. of 0.823, whereas the refined re-distillate had spec. gr. 0.821. The yield of crude kerosene distillate was 80%, while after redistillation the figure was 67%.

As a general rule, protoparaffins are obtained with this apparatus, semi-translucent paraffin-bearing solar oils, further (kerosene) and benzine. However, if the distillates which have formed in the first dephlegmator chambers are subjected to another distillation they break up in the above relationship into kerosene and benzin as well as heavy distillates.

100 m mineral oil residues furnish:

Kerosene	67 m.
Loss of Distillation	26 "
Refining losses	3 "
Residues from second distillation	4 "

The résumé of the opinion rendered by the experts upon the Aleksejeff distillation method reads as follows:

The distillation process is simple, it preceeds smoothly, quietly and continuously, and is not in need of strict attendance and supervision. However, the service is too costly compared with the customary equipment, since the dephlegmator chambers absorb a good deal of heat. Also the yield of the apparatus per unit of heating surface is lower than in the older processes, since these have to heat only 100 parts of the distilling liquid while 30 parts have to be evaporated in order to furnish 30% distillate, whereas the Aleksejeff apparatus has to heat 380 parts oil, while 372 have to be evaporated in order to result in 72 parts of distillate.

Yet, in spite of that, this apparatus caused and attracted a good deal of attention since it pointed the way towards more rational working of the heavy mineral oils and for lubricating oil manufacture from mineral oil residues; but it could not retain its place. However, the basic idea was not lost, indeed, it was received ten years later in a more refined form in the Ragosin method.

Ragosin also found a theoretical basis for his method in that he went to the study of the formation of mineral oils

in the interior of the earth. The underlying cause was the strikingly great difference between the chemical and the physical natures of mineral oils coming from one and the same field. Presupposing the organic origin of petroleum, a satisfactory explanation for this phenomenon can be sought and found solely in a subsquent alteration of the [fol. 863] primary oil. If the primary mineral oil has become subsequently the subject of thermal action, then oil vapors would be evolved therefrom, with the result that pressure is exerted by these vapors both from the liquid as well as upon the surrounding rock containing the deposit. The cracks in the earth caused by the pressure or by other geological influences form the conduit to another new container, as it were, for the secondary deposit.

If the heating of the oil in the first reservoir continues after all of the oil above the crack in the earth has passed into the second reservoir, it follows that through these cracks and crevices naturally also the vapors and gases evolved from the balance must find a way to the second reservoir. By penetrating the whole layer of liquid located in the upper reservoir, these gases induce or initiate a distillation. But if also the second reservoir becomes heated, then a breaking up of the hydrocarbons will be the result.

This cleavage or breaking-up process continues as long as the tension of the oil vapors in the first container is higher than that in the upper one, a factor that naturally is governed also by the temperature of the upper container; and since furthermore the second reservoir may have different temperature at different points of the same, it follows that the highest point served at the same time as a condensing point for the oil vapors. Hence, dephlegmation was occasioned, and by this circumstance the difference in the vapor tensions of the lower and the upper reservoir could be more readily maintained, while the progressive movement of the oil vapors from the lower to the upper reservoir continued for a prolonged period of time.

When the oil in the upper reservoir cooled off entirely, only so much of the mineral oil remained unchanged as there was gas lacking for causing the same to break up. However, the degree or the extent of the breaking-up process is related with the duration of the process, the size of

the mineral oil deposits contained in the first reservoir, and the temperatures prevailing in the two reservoirs. Upon these factors is dependent also the quantity of oil which was produced at a lower temperature in the second reservoir as primary oil.

The benzin and kerosene contents of the various mineral oils as well as the properties of the residues furnish an approximate measure and clue for the degree of the cleavage process produced in the primary oil. (It may be mentioned at this juncture that a simpler and probably better [fol. 864] argued theory for the differences in mineral oils, even for those proceeding from neighboring deposits, is furnished by Engler; he ascribes these discrepancies to slowly proceeding self-polymerization of the lighter hydrocarbons of the primary mineral oil (protopetroleum). In favor of this assumption are also the observations of the author who has found self-polymerization not only with mineral oil distillates, but also in the products of hard coal and lignite tar distillation).

After the mineral oil on account of geological events was brought closer to the surface of the earth, and after it was covered merely by layers which were permeable for gases and vapors, it naturally had to lose gradually its lighter components, with the result that it became heavier. However, the total content of the lower mineral oil reservoir would pass over into the upper one since part of the mineral oil and of the gases which we-e causative for the shift of the oil, was lost.

Now, it was these cosmic phenomena and events after which Ragosin patterned his apparatus (see Figs. 17 to 21). The two boilers A and A′ built with brickwork on top of each other represented, as it were, the reservoirs for the primary and the secondary (split) mineral oil. Since the natural deposits of mineral oil are usually inclined at an angle with relation to one another, Ragosin chose a similar position for his containers, in such a way, that the ends nearly come to touch at one side, while they diverge at the other. The connecting point *u* serves to allow of the passage of the oil vapors from the upper part of the lower boiler to the upper part of the upper boiler, and is arranged at that end of the boiler which is most contiguous

to the upper boiler. At this place there is the second connecting tube *i* whereby the lower part of boiler A_1 is joined with the lower part of boiler A. By means of a cock B this communication can be interrupted ad lib.

Fig. 17.

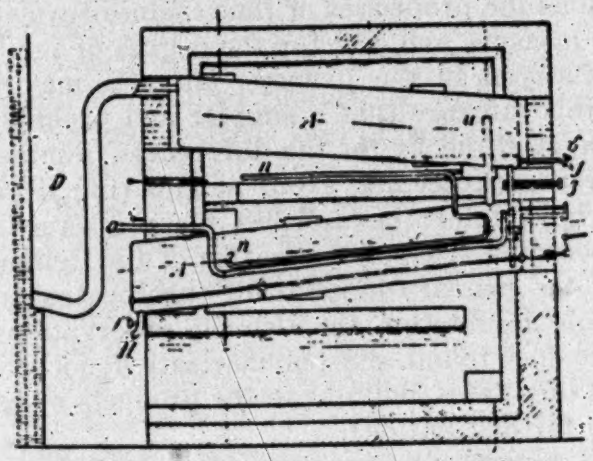


Fig. 18.

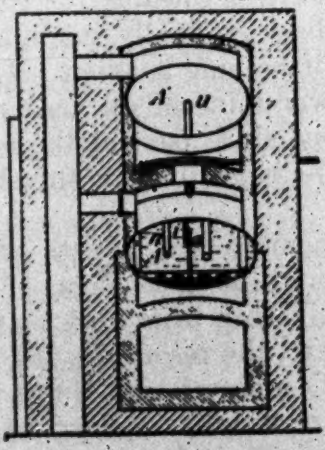
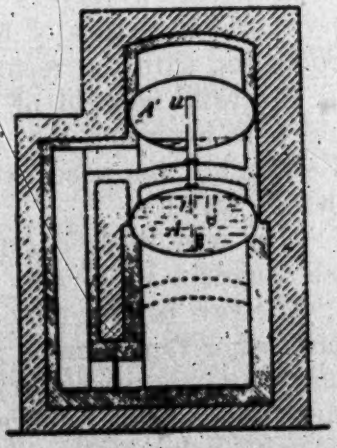
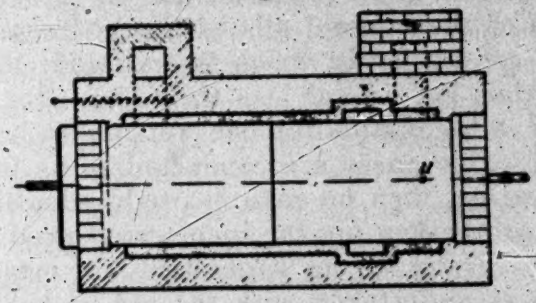


Fig. 19.



[fol. 865] The combustion gases first pass around the lower boiler A, and after they have there yielded the major part of their heat, they may either circulate around the upper boiler, or they may be conducted directly to the smoke stack. Under all circumstances, the temperature of the lower boiler is higher than that of the upper boiler.

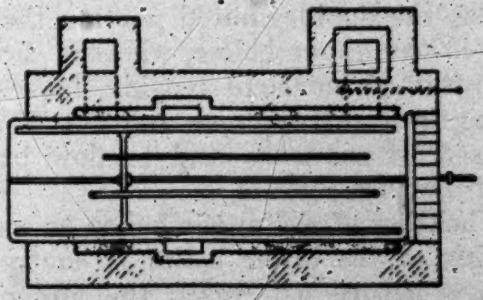
Fig. 20.



The raw material to be broken up, that is, heavy mineral oils or residues thereof, are fed into the lower boiler A through pipe *a* from a tank. The disposition of the oil inlet is so chosen that in the boiler A the level of the liquid is kept constant, so that the distillation can proceed continuously.

The admission of the benzin vapors is effected by way of pipe *n*. To drain out the asphaltum accumulating gradually in the lower boiler, there is used a drain pipe H with cock P, by way of pipe *j* with cock *o'* The overflow pipe D is connected at the highest point in the upper boiler A_1, and the same serves to conduct the oil vapors for fractionated separation into the columns to be described further below.

Fig. 21.



[fol. 866] Now, while the oil vapors from the lower boiler are reaching the upper boiler through connecting pipe *u* they undergo a breaking-up process. That part of the vapors which has a higher tension than atmospheric pressure, leave the boiler through pipe D, whereas the other part in the upper boiler dephlegmates and is allowed to flow back through connecting pipe *i*, when the cock is open, into the lower boiler, where it becomes subject to renewed dissociation.

In this process there is caused merely a cleaving or breaking-up of the mineral oils of the hydrocarbons, that is to say, a conversion in which these liquids become specifically lighter, but do not lose their character as hydrocarbons. If in the distillation one works with light benzin, and if the heating gases are conducted so as to cause no local overheating, then no coke is produced while the hydrocarbons are broken up, the inspisented products in the lower boiler furnishing an asphaltum-like mass. But if this process is undertaken with the aid of heavy benzin, also the decomposition products of asphaltum become mingled with the dissolved vapors of naphthenes and boundary hydrocarbons, whereby a partial disintegration into the elements C and H is caused, and this process naturally is attended with separation of coke, the coke being obtained in the form of a fine dust.

Let us suppose that the tube through which the oil vapors are carried away from the upper boiler, does not lead to the column or the condenser, but that it extends a certain distance while gradually rising. If, then, the upper boiler were left unheated, the liquid would dephlegmate without being broken up, with the result that the same hydrocarbons are obtained as in the lower boiler, in other words, a primary product. But if also the upper boiler is heated, breaking up of the oil vapors will be producted in these, the dephlegmated portion thereof collecting gradually in the upper boiler, whereas the other part, after having attained sufficient tension, leaves the boiler. Due to the length of the distance and due to cooling it is [fol. 867] caused to condense and to flow back into the boiler where it likewise collects.

Now, if the heating of the upper boiler be ceased so that only the heating of the lower boiler is continued, vapors also of primary nature will reach the upper boiler, but without undergoing dissociation, so that the boiler A_1 contains then two kinds of vapor, that is to say, from liquids which have been broken up by heat, and from liquids which have not suffered any changes.

By alternatively heating and cooling of the upper boiler, it is easy to produce at will a mixture of primary and secondary mineral oils which, upon continued heating of both boilers until the end of the distillation, consists predominatly of mineral oil.

The advantage of benzin vapor distillation as contrasted with the use of superheated steam consists first in the dissolving power of the benzin with reference to the hydrocarbons in mineral oils. In vaporous state, the mutual dssolving power is further increased, but in spite of that it can be confined to the oil-like ingredients of the mineral oil by the use of benzin. It is possible in this manenr to eliminate the easily decomposable asphaltum-like bodies, and to prevent their decomposition.

However, in order to carry out the process in a successful manner it is necessary to use a certain minimum quantity of benzin in order that the vapor mixture which distils over and consists of benzin and heavy oil vapors, may preserve sufficient tension in order to overcome outside pressure. The amount of benzin empirically ascertained by Bagosin is 60% of the quantity of oil to be distilled over.

This figure is more satisfactory when compared with the quantity of superheated steam which is ordinarily used and which bears a relationship to the quantities of oil distilled over of 1 ; 1, 6 : 1, and towards the end of the distillation even 21 : 1.

How little heat furthermore is required for the distillation of various mineral oils with ben-in, can be seen from the following working result found by Ragosin.

If the heat capacity of oil is supposed to be—0.55 and the heat of evaporation = 110, we find that for spec. gr. of the raw material:

	0.870	0.906	0.950	0.970
Temperature	260	310	390	410
Calories	253	280	325	335

[fol. 868] Hence, the mean temperature is 300° C, in other words, for each 100 parts by weight of raw material, there is required a quantity of heat sufficient to vaporize about 47 parts water. And this quantity of heat is furnished by 0.7 kilo fuel oil, in other words, the fuel consumption amounts to 5% of the quantity of mineral oil to be worked, or 1/5 of the quantity of fuel otherwise needed.

Experiments frequently repeated show that a mineral oil which has been distilled up to 300°, when heated to 350°

again evolves oil vapors. Hence, by raising the temperature by 50°, the liquid is not only broken up, but is also dissociated, into elements by which coke is incidentally formed. It can be seen therefrom that for breaking up mineral oils a still lower expenditure of heat should be sufficient.

The breaking up of the oil vapors, in other words, after the heat has already been consumed which is required in order that the particles of the liquid may be placed in the condition where mutual repulsion takes place, therefore can not require a higher temperature than what is sufficient for the direct breaking up of the liquid.

The splitting up proceeds in the Ragosin apparatus not intermittently, but progressively. This seems to be indicated also by the circumstance that even in the presence of slight superheating of the oil vapors the heavy fractions consisting of hydrocarbons of higher molecular composition, are split not directly into kerosene, but into ozokerit, while being decomposed into liquids of simpler molecular composition only after repeated heating or upon application of a higher temperature.

In controlling the breaking-up temperatures we have a means adapted to convert heavy mineral oils into all kinds of derivatives starting from the gases answering the formula C_nH_{2n} as far as the liquids of different properties and solid bodies of the same composition. The fact that no elementary decomposition takes place can be proved by experiment.

The favorable effect of the use of benzin in the Ragosin distillation process is explained by Zaloziecki in the following manner (see "Theoretical considerations of the Ragosin distillation method"):

If one takes into consideration the views respecting the evaporation of simple mixtures which have been explained both theoretically and experimentally by Konowaloff (see Wiedemann's Annalen, Vol. 14, 1882, p. 24), we can distinguish between the following types:

[fol. 869] Type I. The vapor of A is readily soluble in B, and the vapor of B readily soluble in A. Then both upon small addition of A to B, and from B to A, the vapor tension of the resultant solution will undergo a decrease. In examining the vapor tension, the vapor pressure of body A upon successive addition of body B will decrease

attain a minimum value, rise thereafter, and finally approach the vapor pressure of B when large additions of the latter are made.

Type II. The vapor of A is little soluble in B, and that of B little soluble in A. Then upon a little quantity of A being added to B, and a little quantity of B to A, the vapor tension of the solution will be caused to grow. By successive addition of B to A the vapor pressure will become greater than that of A in pure state, will attain a maximum, and finally, upon large excess of B, it will drop again and approach the value peculiar to B.

At the beginning of the distillation of residue which contain still a considerable proportion of medium and heavy oils, the benzin vapor may be supposed to possess considerable solubility, and vice versa; hence, the distillation is initiated according to type I, and although the vapor tension decreases it is still high enough to separate these comparatively volatile components.

In proportion as these components are eliminated, the residue gradually loses the dissolving power for benzin vapors, with the result that the distillation changes from type I to type II. The consequence of this change is a rise in vapor tension and this allows also of the evaporation of the more difficulty boiling ingredients, that is to say, of the protoparaffin, without undue increase in temperature. As the distillation proceeds further, the vapor tension ranges around the maximum, hence, it preserves a higher value than is peculiar to even the benzin at this temperature, and takes the place of an increase in temperature which towards the end of the distillation gives rise to decomposition.

This successive rise of the vapor tension which proceeds at the same rate as the successive evaporation of the volatile components constitutes, as it were, a regulator of the distillation which affects the distillation temperature in a favorable sense till the very end of the operation. The distillation will proceed at a so much lower temperature, the higher the vapor tension.

In a comparison between steam distillation and benzin distillation, primarily this circumstance has to be consid- [fol. 870] ered that aqueous vapor has an equally low dissolving power for all components of mineral oil residues,

so that the process from beginning to end proceeds accordng to type II.

The situation is totally different in benzin distillation of the kind resorted to in connection with the use of the Ragosin apparatus. What is decisive in rating the same are the mutual solving conditions of the vapors in the corresponding liquids; the situation may appear somewhat complicated in this case, for the components of the residues will not exhibit any such uniform behavior towards benzin vapor as towards benzin vapor as towards aqueous vapor. It is to be taken as granted that benzin vapor is easily dissolved in petroleum distillates, and also as regards heavy oils a high grade of solubility may be assumed; it is likely that the same decreases in upward direction, and will probably be smaller for paraffin than for the middle of the series of mineral-oil hydrocarbons.

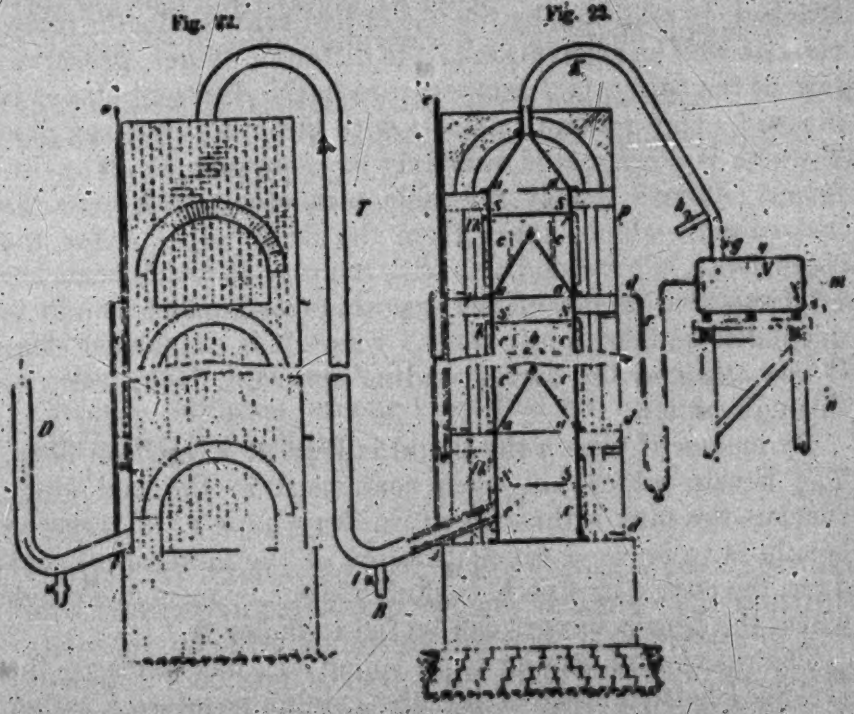
As to the asphaltic components, low solubility with reference to benzin vapor can be taken as granted from the outset, and it is further probable that the heavy ingredients of the residues (protoparaffin) in mixture with asphaltums will be found to be difficulty soluble for benzin vapor.

The difference in the distilling products in benzine vapor distillation has probably to be ascribed to the avoidance of decomposition and extensive separation of the distillates in the Ragosin distilling apparatus. As can be seen from Ragosin distilling apparatus. As can be seen from Ragosin's examples, the distillates are divided into two groups, which, when working without decomposition, are about equally large, to be more precise, into paraffin-free distillates, and a protoparaffin mass having a melting point of about 40° C.

Nothing would be farther than the assumption that oil distillates which are related to kerosene, originate from decomposition; on the contrary, they are contained originally in the residues, similarly as protoparaffin which proves that in this kind of distillation the decomposition is avoided as far as feasible, and that the volatile components of the residues in intact condition (oils and protoparaffins) are separated from the non-volatile ingredients.

The separation of the distillates into practically serviceable groups, to be true, is a matter to be solved by a properly designed condenser; but without genzin vapors it

would not be possible to the same extent, in other words, it is only by virtue of the mixture of the distillate vapors with benzin vapors that the proper conditions for good [fol. 871] separation in the different chambers have been created. However, in order to be practiced in a successful manner, the distillation must be undertaken with an excess of benzin vapor in the dephlegmator space. The construction of the condenser repeatedly referred to before is shown in Figs. 22 and 23.



[fol. 872] The riser pipe D from the upper boiler which conducts the oil vapors from the boiler into the condenser is bent downwardly, being provided at the lower curbed bend with a cock for draining residues of liquid. The apparatus as well as the pipe are protected against chilling by being built into brickwork or by insulation.

The apparatus itself is built up in stages which are formed by sheet sheels. At their ends they are interconnected by means of angle irons thereby forming a columnar structure. Between pairs of stages there is a funnel-like insert piece which tapers in upward direction into an open-

ing *b*. The cone at some distance has an iron dish *s* upon supports *o*. Pipes *d* are bra-ched off at the lowermost point in each stage, and through these the condensates are run off. The upper part of each stage is surrounded by an annular pipe *k* having small downwardly directed apertures, whereas in the lower part there are provided annular chan-*e*nls for running off the water, the latter being supplied to the different cooling spaces by way of pipe *e*.

The column is built into brickwork in such a manner that by the removal of a few bricks any of the stages can be reached; in addition, by the use of bad heat conductor materials as well as separation of the different stages, preservation of the convenient temperature in the different stages is insured. One column connects with the other by riser pipe T which is constructed similarly as riser tube D. The different columns closely resemble each other except for the last column which, apart from the drain pipes *d* for the condensate, is provided also with the pipe K which branches off from the funnel of the top stage and which conducts uncondensed benzin into tank N where it is condensed after it has attained the corresponding spec. gr., being run out through pipe *n*.

By means of pipe *n* the liquid is kept at a constant level. The benzin which has been condensed in the last stage reaches the tank *n* through drain *drain* pipe *r*. If gaseous benzin is to be used for distillation of the mineral-oil residues, the cock *g* in pipe K is shut, while *h* is opened through which the benzin vapors can be fed to boiler A.

The oil vapors issuing from boiler A_1 when reaching the [fol.873] bottom stage of the first column posseses a rather high velocity which is reduced by friction with incidental conversion of mechanical work into heat. At the same time the heavy vapors are condensed and latent heat is liberated with the result that such products as are still in vaporous state are further heated and are caused to flow to the stage next above. This process recurs in each stage, and the distillates of gradually lower spec. gr. are also condensed. The fractionation attained goes as far as 0.002 of the spec. gr.

If the openings designated by *p* in Fig. 22 are exposed, the outside air is allowed to reach the iron shell of the column and thus occasions more rapid cooling. The cooling can be further intensified by water admission to pipes *k*, and the quantities of the condensates in the various stages can be

substantially increased. It will be evident that this is possible only with an incidental sacrifice in the precision of fractionation.

The fundamental principle of this condenser, as will be seen, consists in that the hot oil vapors do not come in direct contact with the column shell before their hear has not been utilized for doing mechanical work. The cooling is not abrupt, hence, also the separation of the different products will be exact.

As regards the productivity of the Ragosin apparatus, this may be cited to get an idea:

100 parts of heavy lubrication oil-goudron furnish:

In the form of residual mineral-oil asphaltums	18%
Paraffin from a 40% mixture with solar oils obtained by crystallization	20%
Kerosene obtained by decomposition	62%
	100%

In the extraction of protoparaffin without breaking up of distillates:

Protoparaffin (ozokerite)	12%
Various distillates (among them fuel oil)	70%
Mineral-oil asphaltum	18%
	100%

The first large-scale tests made abroad were undertaken in a Hungarian petroluem refinery in 1898. The apparatus there used had the following dimensions: diameter of lower cylinder 1500 mm., length 5400 mm., free heating surface [fol. 874] 25 sq. meters, capacity 16000 to 17600 kilos oil. The upper cylindrical boiler was provided with a flame tube of 600 mm. diameter, and at a length of 4800 mm: it had an overall diameter of 1200 mm. The heating surface was 27 sq. m. The dephlegamator column which served to isolate the distillates into 24 fractions had a capacity of 60 cubic meters.

The working results obtained have not yet been brought to the knowledge of the public, still, according to what I have learnt from private sources, they have turned out promising. (See in this connection "The Ragosin distilling

process", by Dr. S. Stransky and A. Gurwitsch, Chem. Revue, 1900, Heft 4 et seq.

We have thus discussed all of the most important types of destructive distillation used in the mineral oil industry. Summarizing the results, it will be seen that the Ragosin method best meets all practical requirements so that, even at this time, it may be pronounced to be the method that is bound to predominate in the near future.

Experiments are undertaken at the present time in a great number of places, and these will do away with such defects and imperfections as the apparatus may still possess, and will tend to put the process upon a firmer basis. The Ragosin process will still offer prospects for continued use even if the situation in the crude oil and the kerosene market should undergo a change whereby the production of illuminating oil by decomposition is rendered superfluous.

The production of undecomposed protoparaffin which in the older plants and working methods is not changed into pyroparaffin (a products of little value), as well as the isolation of natural asphaltums contained in mineral oil offer good prespect even with changed market conditions.

IV. Chemical Properties of Decomposition Oil

The difficulties which attend an exact investigation of the chemical properties of the hydrocarbons making up mineral oils become considerably greater as soon as the investigation relates to complicated members of mineral-oil residues.

For it will be remembered that the residues of petroluem distillation constitute such a complicated mixture of the most different high-molecular hydrocarbons that the standard means of conventional organic analysis are not able to throw any light on to it.

The main difficulty resides in the extremely ready decomposition and breaking up of the hydrocarbons to be investi- [fol. 875] gated in the attempt to isolate them from the mixture. This accounts for the fact that his field has so far been left relatively unexplored.

It was only in the last few years that some interesting works by Engler (Graemer and Spilker, Zaloziecki, Thorpe and Young, and others who have tried to tackle this relatively refractory material some more light has been shed on their properties.

[fol. 876] PETITIONER'S EXHIBIT No. 119

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X. The Decomposition and Genesis of Hydrocarbons at High Temperatures. I. The products of the Manufacture of Gas from Petroleum

By Henry E. Armstrong and A. K. Miller

1. A preliminary account of our work was given to the Society in June of last year (Chem. News, *49*, 285), a somewhat lengthy description of the manufacture of gas from oil, as practised in this country, having been previously [fol. 877] communicated by Dr. Armstrong to the Society of Chemical Industry in a paper read before their London Section in April, and printed in their Journal for September, 1884 (pp. 462—468).

2. The investigation was commenced several years ago, and was carried on almost uninterruptedly during 1884 and the first half of 1885, but the products are so numerous and their separation and identification is attended with such difficulty, that the progress made is far from satisfactory. Nevertheles, a stage has been reached at which it appears desirable to record the results, as they are in part highly suggestive and will lead to new inquiries being undertaken; besides which the methods at our disposal are scarcely sufficient to enable us to unravel the very tangled skein which the investigation presents. An abstract of the

present paper is given in the number of the Abstracts of the Proceedings of the Chemical Society for June 18th, 1885.

3. The products of the manufacture of oil-gas are historically of great interest, as their examination led Faraday, in 1825, to his momentous discovery of "Bicarburet of Hydrogen," now known as benzene.* Another new compound described in the same paper was obtained from the most volatile portion of the condensed liquor from the oil-gas receivers. According to Faraday's analysis, it contained carbon and hydrogen in the same proportions as olefiant gas, but was of double the density. This is the composition of butylene, the discovery of which has therefore always been attributed to Faraday; we shall have occasion later on to consider whether the evidence he adduces is sufficient to warrant this conclusion,

Faraday's memoir affords a considerable amount of information which we think justifies the inference that the oil-gas of the present day differs but little from that then made, although the oils now used are derived from shale and petroleum and it was then customary to use fish or vegetable oil.

4. We have not been able to ascertain that any attempt has been made to add to our knowledge of the chemistry of the subject since Faraday's investigation was published, [fol. 878] notwithstanding the attention paid within recent years to the manufacture of oil-gas, excepting that Greville Williams appears to have commenced the examination of the by-products of its manufacture not long after Dr. Armstrong had begun to study them (Chem. News, 1884, p. 197; see also Jour. Soc. Chem. Ind., 1884, p. 462).

5. In describing our work we propose to disregard the order in which the various constituents were separated or identified; our main object being to throw light on the nature of the changes resulting from the decomposition of petroleum hydrocarbons at high temperatures, it will be desirable to give a connected account of the observations relat-

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* "On new compounds of carbon and hydrogen, and on certain other products obtained during the decomposition of oil by heat:" a paper read June 16th, 1825, by M. Faraday, F.R.S., &c., Phil. Trans., 1825, 440—466.

ing to each of the series of hydrocarbons which occur in one or other of the products examined, viz, the compressed gas itself; the liquid deposited during compression of the gas, either in a chamber attached to the compressing pump or in the reservoir in which the gas is stored; and the tar which is deposited from the crude gas prior to compression. In this paper, however, we shall deal only with that portion of the gas which is absorbed by bromine and with the steam-distillable portion of the tar.

I. Benzenoid Hydrocarbons

6. The liquid deposited during compression of the gas is wholly volatile in steam when recently obtained, and consists of hydrocarbons capable of being polymerized by sulphuric acid, benzenes and a relatively very small proportion of hydrocarbons unattackable by sulphuric acid; the last-mentioned constituents are present in larger quantity in the steam distillate from the tar.

7. On mixing either liquid with moderately dilute sulphuric acid (2 vols. acid 1 vol. water) much heat is developed, and by its action the unsaturated hydrocarbons are for the most part converted into compounds which are not distillable in steam; in order to effect as complete a conversion as possible, it is desirable when the action appears to be at an end to separate the acid from the oil and to treat the latter with stronger acid—4 : 1. In dealing with small quantities a glass stoppered bottle is used; but for large quantities it is well to use a copper can with a tightly fitting metal plug: there is then no danger of the vessel bursting, and it is much easier to quickly cool the mixture. The acid should be added in small quantity at first, and care should be taken in agitating; in working with large quantities it is desirable to steam-distil as soon as the treat- [fol. 879] ment with 2 : 1 acid is at an end, and to well mix the distillate with the stronger acid, as owing to the viscid character of the product it becomes very difficult to complete the conversion of the unsaturated hydrocarbons into polymerides.

The steam distillate finally obtained has a peculiar characteristic unpleasant odour, due apparently to the presence of volatile products of the action of the acid.

8. A large quantity of benzene may be directly crystallised out from the product so obtained from the liquid de-

posited from the gas during compression in the manner first described by Faraday and made popular many years later by Mansfield. We have employed a very simple apparatus for the purpose, consisting of a cylindrical vessel, closed only at the bottom, 12 inches high and 4.5 inches in diameter, made of brass 1/16 of an inch thick; into this fits fairly closely a similar cylinder, the bottom of which has numerous fine holes bored through it. The larger cylinder is placed in a wooden pail or tub, surrounded with a good freezing mixture, and the hydrocarbon is then poured into it; the walls of the cylinder soon become coated with crystals, which are detached by means of a stout metal rod, and this is frequently used in stirring the contents of the cylinder. When crystallisation is complete, the smaller cylinder is pushed down upon the crystalline pulp, the pail is placed between the jaws of an ordinary long carpenter's cramp, a block of wood is placed across the mouth of the inner cylinder, and pressure is gradually applied by turning the screw of the cramp. The expressed liquid is syphoned off as it rises into the interior of the cylinder. Pressure having been applied to a sufficient extent and during a sufficient length of time, the screw is released, the ram withdrawn, the cylinder lifted out of the freezing mixture, and the small amount of liquid floating on the solid cake is poured out; the benzene is then caused to melt by lowering into it a tube fitted up after the manner of a wash-bottle, through which steam is being passed.

If the mother-liquor from the crystals be fratctionally distilled, and the portions boiling near to 80° be then treated as above described, a further considerable quantity of crystalline benzene may easily be obained.

In like manner the lowest fractions of the product obtained on agitating the steam distillate from the tar with acid, &c., also yield benzene.

The benzene thus separated is by no means pure, and [fol. 880] should be treated with alkaline permanganate, bromine, or sulphuric acid, fractionally distilled, and again crystallised.

9. As much of the benzene as possible having been removed, the residue is now extracted with hot concentrated sulphuric acid, and the benzenes are recovered from the solution by hydrolysis (Chem. Soc. Trans., 1884, 148).

The acid should be placed together with the hydrocarbon in a vessel which can be closed—a stoppered bottle if a moderate quantity is to be treated, or a copper can if the quantity be large. To ensure intimate contact, the vessel is then very vigorously shaken. In the first instance cold acid may be used, as heat is developed by the dissolution of the more easily attacked hydrocarbons; afterwards the mixture of acid and hydrocarbons should be heated to 60—70°. An insufficient quantity of acid is used in the first treatment, and the unattacked hydrocarbon is afterwards shaken with fresh acid; finally it is violently shaken with weakly fuming acid in order to remove all the benzene. Care must be taken in doing this, as the action of the fuming acid usually gives rise to the production of gas—sulphur dioxide.

10. The residual unattacked hydrocarbon is then mixed with a little alkali and steam-distilled; the product is a brilliant colourless liquid, having the pleasant sweet odour characteristic of a pure paraffin.

11. On hydrolysing the crude mixture of sulphonic acids, after the whole of the benzenoid hydrocarbons have been recovered, a considerable amount of black carbonaceous matter remains with the acid; we have always regarded this as formed from products of the polymerisation of unsaturated hydrocarbons by the dilute acid during the first treatment.

12. The method described is that which renders it possible to separate the whole of the benzenoid hydrocarbons from the original oil-gas products. Much of the benzene may, however, be obtained without destroying the unsaturated hydrocarbons by refrigerating the appropriate fraction of the liquid deposited on compression of the gas or of the steam distillate from the tar. And it is scarcely necessary to point out, that either separate fractions of the original crude materials, or the crude materials as a whole, may be submitted to treatment in the above manner.

13. To separate the various constituents of the complex mixture of benzenoid hydrocarbons thus obtained, it is fractionally distilled. From the lowest fraction a considerable amount of benzene may easily be frozen out. To separate [fol. 881] the toluene, the fractions boiling below 115°, from which no more benzene can be obtained by refrigera-

tion, are shaken with hot concentrated sulphuric acid: as benzene is less readily attacked than toluene, it is possible by fractional treatment with the acid to dissolve chiefly the latter, leaving a residue from which a further quantity of benzene may be crystallised out. The mixture of sulphonic acids with sulphuric acid is poured into water, the solution neutralised with whiting paste, and the resulting calcium salts are then converted into potassium salts, &c.,; the liquid when sufficiently concentrated deposits a large crop of the characteristic crystals of potassium toluene-parasulphonate, which are recrystallised and hydrolysed to recover the toluene.

14. The xylenes were separated by Jacobsen's method (Ber., *10*, 1009) from the fractions boiling at 135—145°. Metaxylene was identified by conversion into its characteristic trinitro-derivative; independent evidence of its presence was afforded by the production of metatoluic acid in large quantity on oxidation of the fractions collected between 135—145° of the original steam distillate from the oil-gas tar. Paraxylene was obtained as sodium paraxylenesulphonate, $C_8H_9SO_3Na{\cdot}H_2O$; and paratoluic acid was obtained on oxidation of the hydrocarbon separated by hydrolysis of this salt. Orthoxylene was separated in the form of the highly characteristic sodium orthoxylenesulphonate, $C_8H_9SO_3Na{\cdot}5H_2O$. The three isomeric xylenes appear to us to occur in the oil-gas product very much in the proportions in which they ordinarily occur in coal-tar xylene, metaxylene being by far the most abundant, and paraxylene the least abundant.

15. Mesitylene and pseudocumene were separated from the fractions boiling between 155—175° by our method of fractional hydrolysis, the hydrocarbon being for this purpose dissolved in sulphuric acid, the solution diluted with water, and steam passed into it at a temperature not exceeding 100—105°. The hydrocarbon thus separated was then reconverted into sulphonic acid; the barium salt of the acid was almost pure mesitylenesulphonate, $(C_9H_{11}SO_3)_2{\cdot}Ba{\cdot}H_2O$, which is a very characteristic salt. The equally characteristic potassium salt was also prepared.

After separation of the main bulk of the mesitylene, the temperature was raised, and the whole of the hydrocarbons present separated by hydrolysis; it was then reconverted

into sulphonic acid, and the latter several times recrystallised from dilute sulphuric acid, as recommended by Jacob- [fol. 882] sen (Annalen, *184*, 198). In this way a considerable quantity of pure pseudocumenesulphonic acid was readily obtained. The hydrocarbon separated from it had a constant boiling point, and the trinitro- and tribromo-derivative prepared from it had all the properties of these derivatives of pseudocumene.

Mesitylene and pseudocumene are, we think, also present in about the same relative proportions in oil-gas tar as in coal-tar, but it is much easier to separate them from the former on account of the absence of basic compounds.

16. The fractions 180–190° and 190–200° were separately converted into sulphonic acid, from which barium salts were prepared; the salts did not crystallise well, separating from a hot solution in an apparently amrophous state. The dry salt was highly pulverulent, and much like barium 1:2:3:5-tetramethylbenzenesulphonate. The salt obtained from the 180—190° fraction was found to contain 23·97, 24·02, 23·81 per cent. of barium Theory indicates the presence of 24·33 per cent. barium in the sulphonate of a hydrocarbon of the formula $C_{10}H_{14}$. The magnesium salt of the sulphonic acid prepared from the 180—190° fraction crystallised well in flat needles, containing 24·6 per cent. water and 5·21 per cent. of magnesium; a salt of the formula $(C_{10}H_{13}SO_3)_2Mg\,8H_2O$ should contain 24.24 per cent. water and 5·33 per cent, magnesium. Magnesium pseudocumenesulphonate was prepared for comparison, and was found to be a very similar salt; it contained 26·32 per cent. of water and 5·56 per cent. magnesium. A salt of the formula $2[(C_9H_{11}SO_3)_2Mg]\,17H_2O$ would contain 26·61 per cent. water and 5·68 per cent. magnesium. A small quantity of hydrocarbon separated from the barium salt prepared from the 180—190° fraction boiled at 178—188°, chiefly at 180—185°. It gave a solid bromo-derivative which, after recrystallisation from alcohol melted at 215°; after repeated recrystallisation the melting point rose to 232.5°. The analysis of an impure portion of this bromide gave 64·59 per cent. bromine, but only 0·09 gram of substance could be used, and probably this contained tribromopseudocumene; the amount corresponding with the formula $C_{10}H_{11}Br_3$ is 64·69 per cent. bromine.

In the barium salt prepared from the 190—200° fraction 23·12 and 23·36 per cent. of barium was found; a salt of the

formula $(C_{11}H_{13}SO_3)_2Ba$ should contain 23·36 per cent. barium.

These facts leave little doubt that at least one benzene [fol. 883] higher in the series than trimethylbenzene is contained in the oil-gas product. Probably isodurene is present, but unfortunately the amount at our disposal was insufficient to enable us to prove this*

17. A large quantity of naphthalene separates from the fractions collected above 200°. After its removal a comparatively small amount of hydrocarbon is left. Benzene being present in such large amount in the oil-gas product, it appeared not unlikely that diphenyl would also occur in them. Notwithstanding persistent efforts to isolate this hydrocarbon, however, we have entirely failed to discover it in the portions boiling between 250—260°. Hitherto, indeed, we have been unable to determine the nature of any of the benzenoid hydrocarbons of higher boiling point than naphthalene; the quantity obtained is very small, and it is impossible to separate a pure substance by distillation.

II. Hydrocarbons of the C_nH_{2n-2} Series

18. The separation and identification of the unsaturated hydrocarbons other than those of the benzenoid series is compassed with difficulty. By determining the amounts of bromine required to saturate the various fractions, it was in the first instance ascertained that not only olefines, but less saturated hydrocarbons were present. Moreover, that there were no true acetylenes among these, that is, hydrocarbons of the form $CH{\cdot}C{\cdot}C_nH_{2n-1}$, at once appeared from the fact that ammoniacal cuprous and argentic solutions were without appreciable action upon the liquid condensed from the oil-gas. This conclusion was confirmed by the observation made both at the Mansion House Station Works of the Metropolitan District Railway Company and at the

*Since this paper was placed in the printer's hands, K. E. Schulze has announced (Ber., *18*, 3032) the discovery of 1 :2 :4 :5-tetramethylbenzene (durene) in coal-tar. It may be added that, in a paper read at the last spring meeting of the Iron and Steel Institute, Dr. Armstrong stated that the oil from the Jameson coke oven contained benzenes different from those in ordinary coal-tar.

Stratford Works of the Great Eastern Company that the gas itself produced but a very small amount of precipitate in an ammoniacal cuprous solution.

19. On warming the crude liquid obtained from the reservoirs in which the gas is stored, distillation at once sets in, [fol. 884] much gas being at first given off; this gas is absorbed by bromine. On steam-distilling the resulting bromide, less than two-thirds passed over as a colourless heavy oil; the residue became almost entirely solid on cooling, and from it a pure substance was readily obtained by crystallisation from alcohol.

In like manner by passing the compressed oil-gas into bromine, a liquid bromide was obtained which was for the most part easily volatile, only about 7 per cent. remaining when oil ceased to distil over; the residue partially solidified on cooling, and from it more than half its weight of a solid bromide was obtained identical with that referred to in the previous paragraph.

The bromide in question crystallised from alcohol in small, glistening plates, exhibiting under the microscope a very irregular outline; it fused at 116°, and volatised with extreme slowness in a current of steam. The percentage of bromine in it, as determined by Volhard's method of combustion with potassium nitrate and sodium carbonate, &c., was found to be 85.99. Hence there could be little doubt that it was a tetrabromide of the formula $C_4H_6Br_4$, the percentage of bromine in which is 85.55. Judging from its properties, the bromide thus obtained is identical with the crotonylene tetrabromide prepared by Caventou from the liquid deposited on compressing coal-gas.

Theoretically, four distinct hydrocarbons of the formula C_4H_6 are possible, viz:

1. Ethylacetylene	CH.CEt.
2. Dimethylacetylene	CMe.CMe.
3. Methylallene	$CHMe.C.CH_2$.
4. Vinylethylene (dimethyleneethane).	$CH_2.CH.CH.CH_2$.

Ethylacetylene is excluded, as our hydrocarbon is not a true acetylene; the hydrocarbon obtained by Caventou from crude butylene bromide gave a tetrabromide which volatilised somewhat readily in the air, and from Almedingen's

experiments there is every reason to suppose that this hydrocarbon was dimethylacetylene (Ber., *14*, 2073). By distilling erythrol with formic acid, Heninger obtained a hydrocarbon of the formula C_4H_6 yielding a bromide similar to that prepared by ourselves and apparently identical with that obtained by Caventou by the decomposition of fusel oil at a red heat and from coal-gas: as this hydrocarbon is formed from erythrol it may almost certainly be regarded as dimethyleneethane or vinylethylene. [fol. 885] On inspection of the four formulæ it will be obvious that a study of the oxidation-products is calculated to afford the required proof: vinylethylene should not yield acetic acid, which would, however, be a product of the oxidation of both dimethylacetylene and methylallene; and ethylacetylene forms propionic acid.

20. To obtain the hydrocarbons for oxidation, we have employed a method which we believe will in the future be of great service in the investigation of unsaturated hydrocarbons. The usual practice is to withdraw the bromine from the bromides of these hydrocarbons by means of sodium, but there are numerous objections to this method: in many cases the change takes place only with difficulty and at a high temperature; in others secondary products are formed owing to the high temperature locally developed; and the sodium usually becomes coated with a protecting layer of bromide. It occurred to us that Gladstone and Tribe's zinc-copper couple might be used with advantage, they having already shown that ethylene and propylene bromides are readily deprived of their bromine by its action in presence of alcohol (Chem. Soc. J., 1874, 406). The results have entirely surpassed our expectations; as in all cases hitherto examined we have obtained a practically theoretical yield of hydrocarbon by merely warming the bromide with alcohol and the couple. Moreover, the hydrocarbon thus recovered has always been found to be identical with that used in preparing the bromide—that is, it again yields the same bromide. Unfortunately this method was not made use of until nearly the close of our experiments; had we known of it earlier, we feel sure that we should have been in a position to throw far more light on the nature of the products of the oil-gas manufacture. We may add that it is our intention fully to

inquire into the application of this method to the separation of unsaturated hydrocarbons from their compounds with halogens.

21. The oxidation of the hydrocarbons separated from the bromide $C_4H_8Br_4$ by the action of the zinc-copper couple was effected by displacing part of a 2 per cent. solution of potassium permanganate from a bottle full of it by means of the gas from 50 grams of the bromide—the gas having been collected over water in a holder and left for some time in contact with the water to remove alcohol-vapour. The permanganate was vigorously shaken to bring it into contact with the gas, and the oxidation being completed, sulphuric acid was added and the volatile acid removed by [fol. 886] steam-distillation. The distillate was neutralized by the addition of about 1.6 gram of sodium carbonate; the neutral liquid having been concentrated, the required amount of silver nitrate was added, and the solution boiled; an amount of silver was precipitated practically equivalent to the silver nitrate used, and no trace of acetate could be detected in the filtrate.

As formic acid is its oxidation-product, there can be no doubt that the hydrocarbon of the formula C_4H_6 from oil-gas is dimethyleneethane or vinylethylene, $CH_2.CH.CH.CH_2$.

22. On steam-distilling the bromides prepared from the fractions of the original liquid from the oil-gas reservoir collected within a few degrees on either side of 40°, dark-coloured viscid residues were obtained in which crystals gradually formed. It was easy to separate these mechanically and to purify them by recrystallisation from alcohol. The pure substance crystallised in long, thin, narrow, well-defined prisms, melting at 115°. Analysis gave results agreeing with the formula $C_4H_8Br_4$; thus:

Bromine	per cent	82.19	Subs. 0.1982	AgBr	0.3828
"	"	82.49	" 0.2210	"	0.4284
"	"	82.53	" 0.2441	"	0.4734
"	"	82.55	" 0.2544	"	0.4935
"	"	82.15	" 0.2083	"	0.4021
Hydrogen	"	2.30	" 0.2278	H_2O	0.0471
"	"	2.31	" 0.2612	"	0.0544
Carbon	"	15.82	" 0.2278	CO_2	0.1322
"	"	15.93	" 0,2612	"	0.1526

		Percentages	Mean results
C_5	59.85	15.47	15.87
H_8	8.00	2.07	2.30
Br_4	319.04	82.46	82.38
	386.89	100.00	100.55

23. The hydrocarbon was separated from this bromide by warming it with the zinc-copper couple and alcohol; the amount obtained was almost the theoretical. After several days' digestion with calcium chloride in a sealed tube it was distilled; it boiled almost constantly at about 45°, leaving a few drops of a syrupy residue which exploded when heated on platinum, in this respect behaving somewhat like isoprene. It had the peculiar alliaceous odour so characteristic of the crude liquid deposited from oil-gas. It was reconverted into the original tetrabromide on careful treatment with bromine. It was readily oxidised by a 4 [fol. 887] per cent. solution of potassium permanganate: more than half of the volatile acid produced was formic acid the rest being pure acetic acid.

Five hydrocarbons of the formula C_5H_8 are at present known: propylacetylene, isopropylacetylene, ethlmethylacetylene, piperylene and isoprene; ours appears to be a sixth. The first three of these are excluded from consideration on account of their behaviour on oxidation; moreover, our hydrocarbon is not a true acetylene, and cannot, therefore, be either propyl- or isopropyl-acetylene. Piperylene, according to Hofmann (Ber., *14*, 665) forms a tetrabromide crystallising from alcohol in glistening plates. Isoprene yields a liquid bromide. Eight modifications in all are possible of a hydrocarbon of the formula C_5H_8; three of these are derived from acetylene; the formulæ of the remaining five are as follows:

CH_2	CH_3	CH_3	CH_3	$C(CH_3)_2$
CH	CH	CH_2	CH	C
CH_2	CH	CH_2	C	CH_2
CH	CH	C	CH	
CH_2	CH_2	CH_2	CH_3	
Allylethylene.	Isoallylethylene.	Ethylallene.	Symmetrical dimethylallene.	Unsymmetrical dimethylallene.

Piperylene, according to Ladenburg (Ber., *16*, 2059) is allylethylene; and that this is not the composition of our hydrocarbon may be inferred from the fact that it yields acetic acid on oxidation. Ethylallene is also excluded as it would furnish propionic acid on oxidation. But three formulæ remain therefore, and we incline to select that of isoallylethylene on account of the simple relation which this hydrocarbon bears to normal amylene, from which probably our hydrocarbon is immediately derived:

$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH \cdot CH_2$ = Propylethylene
$CH_3 \cdot CH \cdot CH \cdot CH \cdot CH_2$ = Isoallylethylene

If our argument be correct, isoprene must be either symmetrical or unsymmetrical dimethylallene; taking into consideration all that is known of the terpenes—to which it is so intimately related—the latter is the more probable. We are now engaged in the study of the hydrocarbons of the formula C_5H_8 in the hope of solving this problem, which is one of considerable importance in connection with the question of the constitution of the hydrocarbons of the formula $C_{10}H_{16}$.

24. A faulty determination of bromine, made by Vol- [fol. 888] hard's method, led us, in the first instance, to regard the bromide just described as identical with Schorlemmer's so-called hexoylene tetrabromide, $C_6H_{10}Br_4$, whose description of this compound tallies very closely with that which we have given of our tetrabromide. Schorlemmer prepared his substance from a fraction boiling at about 80° of the more volatile products of the distillation of boghead cannel; to this he added bromine in excess, and after removing the greater part of the admixed benzene by distillation, he heated the bromide with sodium to regenerate the hydrocarbon; this was again brominated. The product was an oil from which the solid gradually crystallised out. It may be mentioned that Schorlemmer bases the formula $C_6H_{10}Br_4$ on a single determination of bromine in only 0·1970 gram of substance. In the hope, therefore, of obtaining hexoylene we very carefully fractioned out a portion boiling at about 80—82° from our crude material, and this was brominated; on steam-distilling the product much benzene passed over, then an oily bromide heavier than water, a

moderately limpid dark-brown oil remaining; no crystals whatever separated from this, and it was therefore submitted to the action of the zinc-copper couple in presence of alcohol. The regenerated hydrocarbon was again brominated and steam-distilled; very little came over. A minute quantity of solid was, however, deposited in the condenser. The experiment was repeated with a considerable quantity of the fractions collected at 70—80°: after adding excess of bromine, the product was steam-distilled until *axab*usted; traces of a solid were again obtained. On extracting the residue with alcohol comparatively little dissolved and no crystals could be obtained from the alcohol extract: the final residue was a carbonaceous mass. The solid referred to crystallised from alcohol in small, hard, well-formed, short prisms melting at 185°; the quantity obtained was too small even for an analysis.

25. In all cases, on steam-distilling the crude bromides from the various fractions, decomposition was observed to take place more or less; and the non-volatile residue from all but the lowest fractions was more or less carbonaceous, and alcohol extracted but very little oily matter, leaving a friable residue. The bromides which are thus decomposed are probably derived from hydrocarbons of the C_nH_{n2-2} series—or in part perhaps from less saturated hydrocarbons—such as Schorlemmer has shown to be present in cannel [fol. 889] oils. The polymerides obtained by means of sulphuric acid were precisely of the character of those described by Schorlemmer (Annalen, 1866, *139*, 244).

III. Hydrocarbons of the Olefine Group

26. Indication of the presence of these hydrocarbons is afforded by the behaviour with bromine especially of the lowest fractions of the "hydrocarbon" deposited during compression of oil-gas; these fractions, if free from benzene, are entirely converted into polymerides and soluble bodies on treatment with sulphuric acid; they therefore consist of unsaturated hydrocarbons, but the amount of bromine which they will absorb is far less than would be the case if they contained only hydrocarbons less rich in hydrogen than the olefines.

To isolate the pure olefines from mixtures such as those with which we have had to deal, no ordinary method will suffice; had we become aware that the zinc-copper couple was applicable to the separation of unsaturated hydrocarbons from their bromides at an early stage instead of almost at the close of this portion of the investigation, it would undoubtedly have been possible to isolate the olefines; but as it was we were obliged to content ourselves with the proof that olefines were present, and with an indirect determination of their nature.

The method followed consisted in oxidising the various fractions by agitation in a stoppered bottle with a cold 4 per cent. solution of potassium permanganate. In selecting this method of treatment we were guided by the knowledge that the normal olefines—those of the type $C_nH_{2n+1}CH{\cdot}CH_2$—are converted by oxidation into acids of the acetic series of the type $C_nH_{2n+1}COOH$, the CH_2 group being eliminated as formic acid; only true acetylenes—i. e., hydrocarbons of the formula $C_nH_{2n-1}C{\cdot}CH$—yield similar products, and, as these were known to be absent from our crude material, the production of the corresponding acid from a fraction of about the boiling point of any particular normal olefine would be conclusive proof of the presence of that olefine. Thus the normal amylene fraction should yield butyric acid, the normal hexylene fraction valeric acid, &c.

The appropriate fractions having been oxidised, sulphuric acid was added, and the volatile acid separated by steam-distillation; the distillate was neutralised with sodium carbonate, concentrated, and then fractionally pre-
[fol. 890] cipitated, with silver nitrate; the silver precipitates were fractionally extracted with water, the solutions well boiled to decompose formate, and the dissolved salts crystallised out and analysed. When a silver salt of constant composition was obtained, it was converted into the calcium salt, as the lower normal primary acids of the acetic series all furnish characteristic calcium salts.

27. The amylene, hexylene, and heptylene fractions treated in this way gave respectively normal butyric, normal valeric, and normal caproic acids.

The higher fractions were similarly treated, but repeated experiments failed to yield any indication whatever of the

presence of olefines higher than heptylene: formic and acetic were the only volatile paraffinoid acids produced—these being associated with the oxidation-products of the benzenoid hydrocarbons present in the fractions examined.

A very careful study of all the various fractions obtained has convinced us that besides the three normal primary olefines above mentioned, no other hydrocarbons of the C_nH_{2n} series, or indeed of any other paraffinoid series, can be present, except such as yield acetic and formic acids on oxidation; and we have no reason to suspect that any olefines other than those mentioned are present in the liquid products from the manufacture of oil-gas: our opinion being that the acetic acid obtained was derived from hydrocarbons less saturated than the olefines.

28. We have already referred to the presence of the hydrocarbons C_4H_8 in the compressed oil-gas (§ 19), and to the manner in which it was separated from the crude mixture of bromides obtained on passing the gas into bromine. On distilling the steam-distillate from this mixture of bromides some hydrogen bromide was evolved, but after a few distillations the constitutent yielding this gas was practically all decomposed. By far the largest amount of the bromide separated by fractional distillation had about the boiling point of ethylene bromide, and a considerable quantity of this compound was crystallised out from this portion of the distillate by refrigeration.

29. The next largest fraction had about the boiling point of methylethylene (propylene) bromide, and we have no doubt that it mainly consisted of this compound, as acetic acid was obtained in large quantity by direct oxidation of this fraction with permanganate.

[fol. 891] 30. Ethylene and propylene having thus been detected in the oil-gas, and normal amylene, hexylene and heptylene in the liquid deposited from it, it was to be expected that normal butylene was also present. A quantity of about 4000 grams of bromides from the gas gave, however, but a relatively small quantity boiling at a higher temperature than propylene bromide, and as it was impossible to separate a pure product by distillation, the various fractions were directly oxidised with permanganate. The quantities used were:

59	grams	boiling at	148—153°
42	"	"	153—158
14	"	"	158—164
51	"	"	above 164°.

The acid distillate was treated with lead oxide in the manner recommended by Linnemann (Annalen, *160*, 222), in order to separate propionic acid, but this acid could not be detected; in fact, only acetic and formic acids were formed.

We have before mentioned that a considerable quantity of bromides was obtained by passing into bromine the gas given off when we began to distil the liquid deposited from oil-gas on compression, and that at least two-thirds of this was volatised on steam-distillation, the residue consisting mainly of crotonylene tetrabromide; it is possible that the portion of the mixture of bromides volatile with water-vapour contained butylene bromide, but most unfortunately the whole of this material was lost in the fire which occurred in the laboratory of the London Institution during the course of the investgiation.

As butylene has a much lower boiling point than crotonylene, we should certainly expect to find its bromide among those obtained from oil-gas itself, as a considerable quantity of crotonylene tetrabromide is present; our failure to detect it has led us to consider the evidence advanced by Faraday upon which the discovery of butylene among the oil-gas products is attributed to him, and we are of opinion that it is by no means exclusive. His words are as follows:—

"If a portion of the original liquid be warmed by the hand, or otherwise, and the vapour which passes off be passed through a tube at O° (Fahr.), very little condensed vapour will go on to the mercurial trough, but there will be found after a time a portion of fluid in the tube distinguished by the following properties. Though a liquid at O°, it upon slight elevation of temperature begins to boil, and before it has attained 32° is all resolved into vapour or gas. • • • [fol. 892] The sp. gr. of the portion I obtained was between 27 and 28, hydrogen being 1. • • • When cooled at O° it condensed again, and inclosed in this state in a tube of known capacity and hermetically sealed up, the bulk of a given weight of the substance at common temperatures was ascertained. This compared with water gave the sp. gr. of the liquid as O 627 at 54°. • • • Alcohol dissolves it in

large quantity. * * * Sulphuric acid condenses the gas in very large quantity: 1 volume of the acid condensing above 100 volumes of the vapour. * * * Great heat is produced during the action, no sulphurous acid is formed; the acid is much blackened, has a peculiar odour, and upon dilution generally becomes turbid, but no gas is evolved. A permanent compound of the acid with carbon and hydrogen is produced, and enters as before mentioned into combination with bases. A mixture of 2 volumes of this vapour with 14 volumes of pure oxygen was made, and a portion detonated in a eudiometer-tube; 8·8 volumes of the mixture diminished by the spark to 5·7 volumes and these by solution of potash to 1·4 volumes, which were oxygen. Hence 7·4 volumes had been consumed, consisting of:

Vapour of substance	1·1
Oxygen	6·3
Carbonic acid formed	4·3
Oxygen in carbonic acid	4·3
Oxygen combining with hydrogen	2·0
Diminution by spark	3·1

This is nearly as if 1 volume of the vapour or gas had required 6 volumes of oxygen, had consumed 4 of them in producing 4 of carbonic acid gas, and had occupied the other 2 by 4 of hydrogen to form water. Upon which view 4 volumes or proportionals of hydrogen = 4, are combined with 4 proportionals of carbon = 24, to form 1 volume of the vapour, the specific gravity of which would therefore be 28. Now this is but little removed from the actual specific gravity obtained by the preceding experiments; and knowing that this vapour must contain small portions of other substances in solution, there appears no reason to doubt that, if obtained pure, it would be found thus constituted. * * * Chlorine and the vapour were therefore mixed in an exhausted retort: rapid combination took place, much heat was evolved, and a liquor produced, resembling hydrochloride of carbon, or the substances obtained by the same process from olefiant gas. * * * Further, it was composed [fol. 893] of nearly equal volumes of vapour and chlorine; it could not, therefore, be the same as the hydrochloride of carbon from olefiant gas, since it contains twice as much carbon and hydrogen."

Taking into account our own observations, especially the fact that we have failed to detect butylene although crotonylene was obtained in considerable quantity, we are inclined to think that Faraday was the discoverer of crotonylene rather than of butylene. It is obvious that he could not have had a pure substance for examination; the ratio of the density of his gas to that of hydrogen was between 27 and 28, and these are numbers which represent the relative density of crotonylene and butylene respectively; the results of his combustion-analysis are almost equally compatible with either formula, C_4H_6 or C_4H_8, always bearing in mind that probably both propylene and amylene were present as impurities; we are not aware that the behaviour of butylene with sulphuric acid has been studied; but it is scarcely probable that it would be so readily absorbed as Faraday describes; there remains but one fact which undoubtedly lends support to the conclusion that it was butylene, viz., that on mixing it with chlorine a chloride was formed, "composed of nearly equal volumes of the vapour and of chlorine." Our proof of the absence of butylene, it should be added, holds good only on the assumption that the butylene present in ethylethylene, as the two dimethylethylenes would yield acetic acid on oxidation. As, however, all the olefines which are proved to have been present are represented by the formula $C_nH_{2n-1}CH{:}CH_2$, it does not appear probable that the butylene would form an exception, especially as the crotonylene which is so abundantly contained in oil-gas is indubitably a derivative of normal butylene.

IV. Hydrocarbons Insoluble in Sulphuric Acid

31. Our method of separating these hydrocarbons has already been described (§§ 7—10). They are contained almost exclusively in the portion boiling above 150° of the steam-distillate from oil-gas tar: for example, about 1800 c.c. of fractions boiling at 105—130° gave after exhaustive treatment with sulphuric acid only 6 grams of insoluble hydrocarbons boiling at about 125—140°.

As far as possible, with the limited amount of material at [fol. 894] our disposal, the attempt was made to separate the mixture into its constituents by fractional distillation; but no very decided separation was accomplished. Three fractions were analysed with the following results:

	160—165°	180—185°	200—205°
Carbon percentage	85.33	85.37	85.27
	—	85.26	85.70
	—	85.63	85.50
	—	—	85.39
Hydrogen percentage	14.80	14.74	14.32
" "	—	14.73	—
Relative density, $\frac{0°}{0°}$	0.7775	0.7886	0.8050
" " $\frac{20°}{20°}$	0.7637	0.7768	0.7980

The general mean of the eight carbon determinations is 85·43 per cent., and of the four hydrogen determinations * 14·63 per cent. These numbers are very nearly those which correspond to the formula C_nH_{2n}, viz., 85.56 per cent. carbon and 14·32 per cent. hydrogen. A paraffin of the formula $C_{10}H_{22}$ contains only 84·47 per cent. carbon and 15·53 per cent. hydrogen; while even that of the formula $C_{12}H_{26}$ contains but 84·67 per cent. carbon and 15·33 percent. hydrogen. The conclusion that our products did not in the main consist of hydrocarbons of the C_nH_{2n+2} type is confirmed by the comparison of our determinations of relative density with the data given by Kraft (Ber., *15*, 1687) for the normal paraffins:

	B. p.	Density at 0°	Density at 20°
$C_{10}H_{22}$	173·0°	0·7452 gram	0·7304 gram
$C_{11}H_{24}$	194·5	0·7557 "	0·7411 "
$C_{12}H_{26}$	214·5	0·7655 "	0·7511 "

Our figures are in every case considerably higher, and the difference would be greater if a strict comparison were made by calculating the densities corresponding to our relative densities. We are satisfied this is not due to the presence of

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*As a warning to those who, like myself, are in the habit of using compressed oxygen for combustions, I may mention that several hydrogen determinations were lost, owing, as was afterwards discovered, to the presence of traces of hydrogen in the oxygen.—H. E. A.

benzenoid hydrocarbons, as special care was taken to remove [fol. 895] these by treatment with fuming sulphuric and nitric acids followed by distillation from sodium.

Our figures more nearly agree with those given by Markownikoff and Oglobine (Ann. Chim. Phys., 1884 [6], 2.372) for the C_nH_{2n} hydrocarbons which they separated—probably in a state of only approximate purity—from Russian petroleum:

	B. p.	Density at 0°
$C_{10}H_{20}$	161°	0.795 gram
$C_{11}H_{22}$	180	0.8119 "
$C_{12}H_{24}$	196	0.8025 "

Hence we are of the opinion that the portion insoluble in sulphuric acid of the steam-distillate from oil-gas tar which we have examined contained both true paraffins and pseudolefines such as mainly compose Russian petroleum, the latter being probably the principal constituents.

V. Summary and Discussion of Results

32. Thus far we have been led to recognise among the products of the manufacture of oil-gas the following hydrocarbons:

a. Paraffins, of which traces only may be said to be present.

b. "Psuedolefines," that is, saturated hydrocarbons of the C_nH_{2n} series such as occur in Russian petroleum; these also are present in relatively small amount.

C. Olefines, viz., ethylene, propylene, normal amylene, nomral hexylene and normal heptylene, all higher homologues being absent. Ethylene is an important constituent of oil-gas as used, and so also apparently is propylene. The liquid deposited from the crude gas on compression is moderately rich in amylene, hexylene and heptylene.

d. "Pseudacetylenes," viz., crotonylene (dimethyleneethane), $CH_2CH.CH.CH_2$, and isoallylethlene, $CH_3.CH.CH.CH.CH_2$. The former is probably an important constituent of the gas, being of high value as an illuminant. Besides these two, both the liquid deposited on compression of the gas and the tar are rich in hydrocarbons identical with, or

very closely related to, those discovered by Schorlemmer in cannel oils.

e. Benzenoid hydrocarbons, viz., benzene, toluene, the three isomeric dimethylbenzenes, the two trimethylbenzenes —pseudocumene and mesitylene—and naphthalene; the first mentioned is a specially important constituent in point of quantity. There is a reason to believe that other benzenoid hydrocarbons besides these are present, even in the portions of the tar volatile with steam.

[fol. 896] 33. We have had the opportunity of examining various samples of the oil—shale oil or crude petroleum—used at the works from which we have obtained our materials, and have satisfied ourselves that the proportion of constituents in them volatile with water-vapour was small, and that they were of a different character from those met with in the bye-products from the manufacture; we have therefore little doubt that practically all the above-mentioned substances are produced in the course of the manufacture of the gas.

34. The paraffins are probably formed in the manner indicated by Thorpe and Young (Proc. Roy. Soc., 1873, *21*, 184), although it is possible that they are in part original constituents of the oil used. It is, however, noteworthy that whereas Thorpe and Young in their investigation of the decomposition of solid paraffins by heat obtained mixtures of lower paraffins and olefines almost in equimolecular proportions from pentane upwards, our material, although rich in amylene and its next two homologues, has not been found to contain the corresponding paraffins.

35. The "pseudolefines" are also more probably products of change than original constituents. But it is to be remembered that according to Beilstein and Kurbatow (Ber., *13*, 2028), American petroleum contains hydrocarbons of the C_nH_{2n} series similar to those in Russian petroleum: hence, assuming our view to be correct, the question arises whether the pseudolefines are formed by simplification of higher pseudolefines or by the removal of hydrogen from corresponding paraffins. Theoretically this question is one of considerable importance, and we are therefore making it the subject of special experimental study.

36. The presence of olefines in products of the distillation of cannel, of coal and of paraffin, has been established by

various observers, but no proof of their nature had hitherto been given; it is therefore a matter of interest that those detected by us are all of the type $C_nH_{2n+1}CH:CH_2$.

37. Regarding the hydrocarbons of the C_nH_{2n-2} series, it is to be noted that vinylethylene is present in much larger proportion than isoallylethylene, and hence it may be inferred that the former is a much more stable compound. Judging from the behavior on oxidation of the remaining unsaturated hydrocarbons, which it is to be assumed are to a large extent also members of the C_nM_{2n-2} series, it appears [fol. 897] probable that they are formed from corresponding normal paraffins by processes similar to those by which these paraffins are converted into normal olefines and by which vinylethylene and isoallylethylene are formed from the corresponding normal olefines or paraffins.

38. Since Bertholot's discovery of the formation of benzene from acetylene, the benzenoid hydrocarbons have always been regarded as built up from true acetylenes (comp. Jacobsen, Ber., *10*, 853). The fact that true acetylenes are all but absent from oil-gas and the bye-products of its manufacture would lead us to doubt whether this is so entirely the case; and the question arises whether these hydrocarbons may not also be directly descended from corresponding paraffins; whether, for example, benzene may not be obtainable directly from hexane by withdrawal of hydrogen. It is sufficient to point this out, and it would be useless to further discuss the question; but we shall endeavour to solve it by experiment.

It will suffice to have pointed out thus briefly the various problems which await experimental investigation arising out of the examination of the products of the decomposition of petroleum hydorcarbons in the manufacture of oil-gas. By continuing the examination of these products, and also by the study of the changes undergone by a material of more definite composition than the oils used for the purpose, viz., solid paraffin, we hope to obtain facts which will serve to elucidate the nature of many of the changes in hydrocarbons which occur at higher temperatures. The subject is one of very great importance, both as bearing on the discovery of rational methods of coking coal and of manufacturing illuminating gas and also hydrocarbons such as benzene, naphthalene and antracene. It has undoubtedly also a bearing

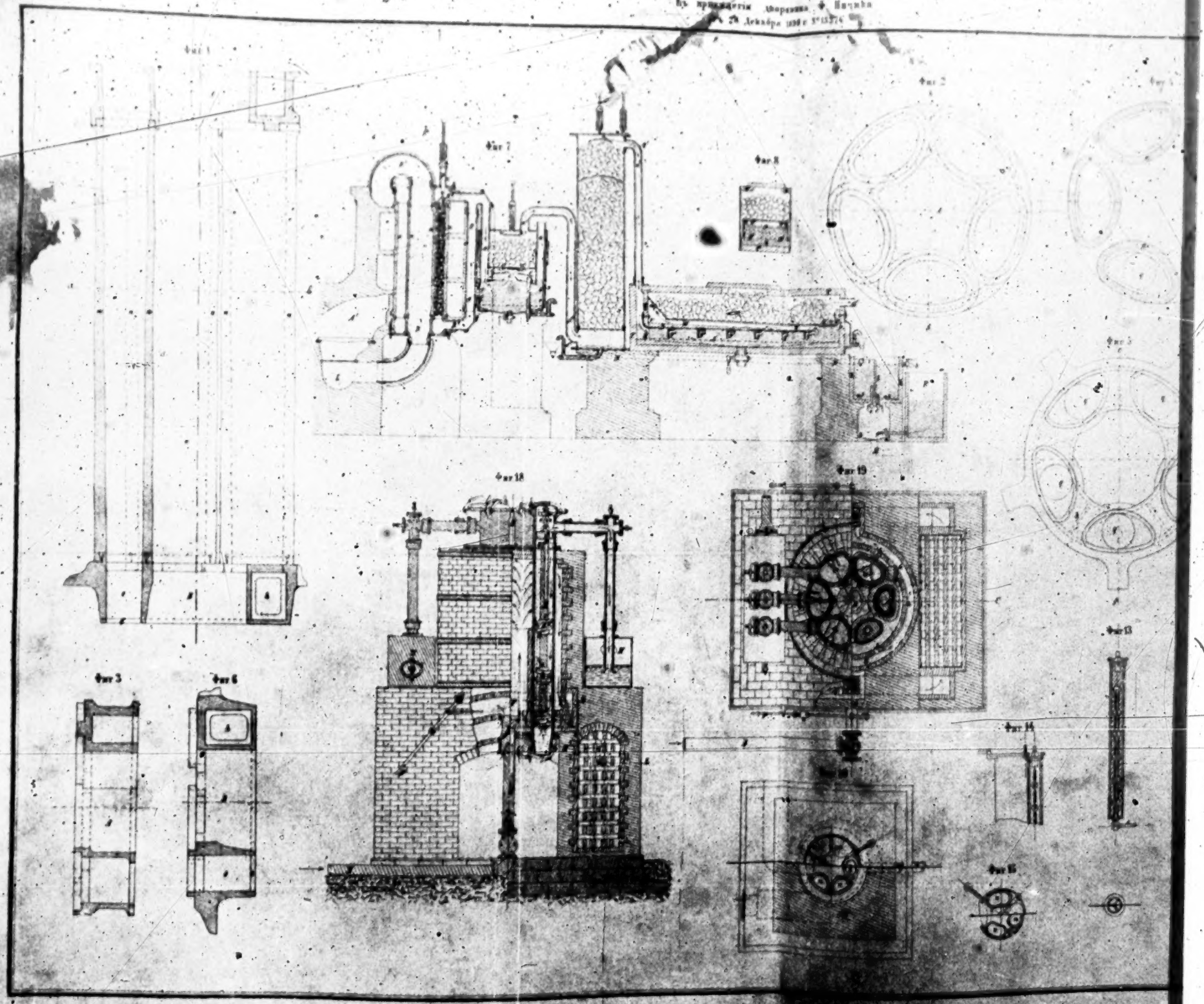
upon the question as to the origin of the complex mixtures of hydrocarbons such as constitute the different varieties of natural petroleum.

Dr. Armstrong has in his previous paper expressed his thanks to various gentlemen connected with the Great Eastern and Metropolitan District Railways for aid afforded him in carrying out this investigation. We desire on this occasion, however, to thank Mr. W. F. Pettigrew, Engineer in charge of the Great Eastern Company's oil-gas works, for his ever-ready assistance during the past year.

City and Guilds of London Institute, Central Institution, December, 1885.

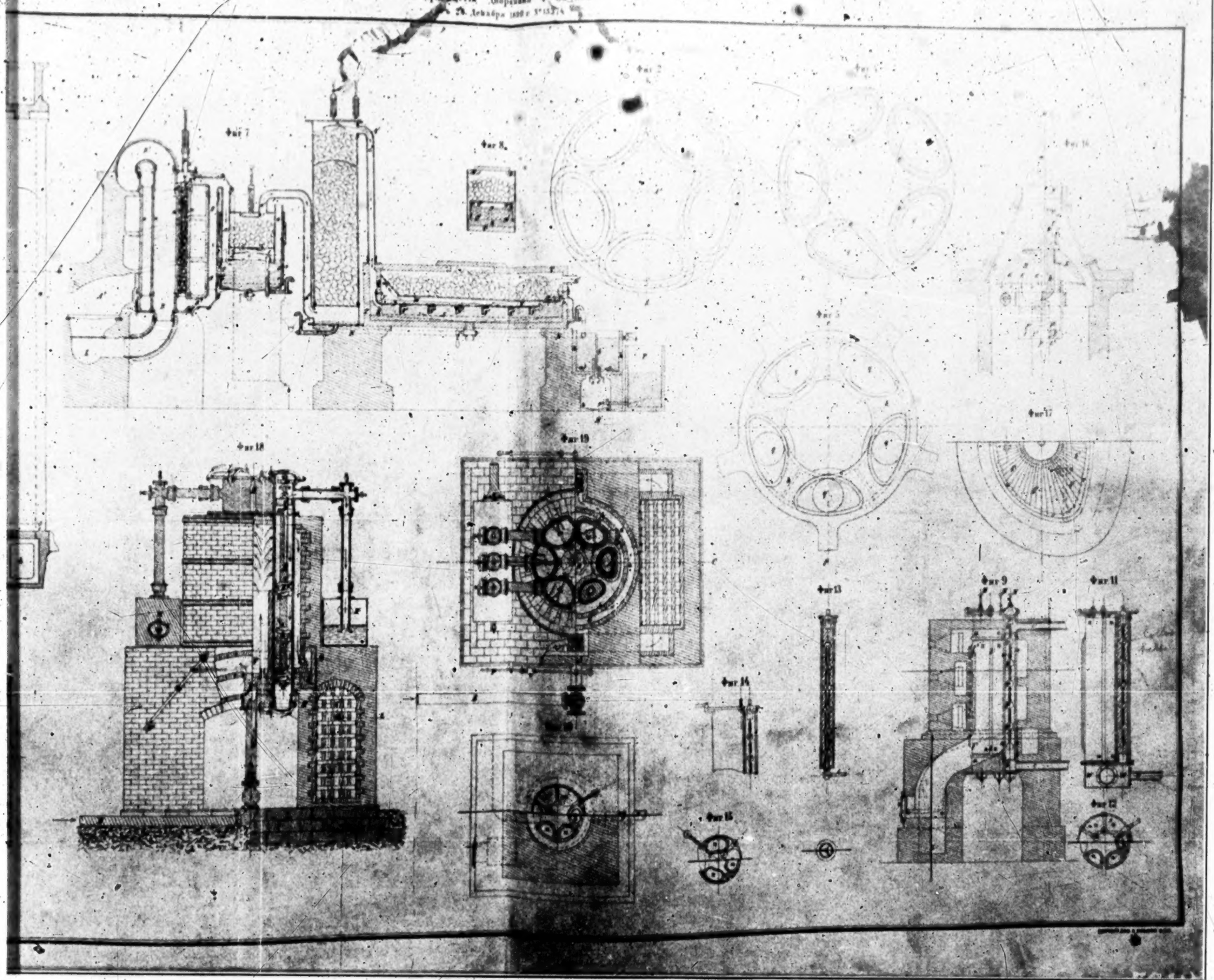
(Here follows Petitioner's Exhibit No. 120, side folio 898)

Къ привилегіи Ф. Нагеля
отъ 28 Декабря 1880 г. № 13276



Рецептовъ-Книжн. No. 120

№ 528.
Къ привилегіи Шорошка и Ивушки
отъ 20 Декабря 1888 г. № 13774.



[fol. 899] TRANSLATION OF PETITIONER'S EXHIBIT No. 120

Russian Patent No. 4584 of 1890

Issued by the Department of Commerce and Manufacture in 1890 to the Nobleman Felix Inchick for apparatus for obtaining illuminating gas from petroleum and petroleum residues.

Technology Engineer Kaupe, and Technologist of the first rank, Checaloff, August 22, 1880, appeared at the Department of Commerce and Manufacture with a petition to issue to the Nobleman Felix Inchick and to the St. Petersburg merchant, Henrick Fennelberg, a five year patent for the apparatus for obtaining illuminating gas from petroleum and petroleum residues, and on the third of April of 1885 and the third of May 1889 have solicited the issue of said patent to Felix Inchick residing at Baku.

The subject of the invention is represented in the following structure of compound retorts for obtaining gas from petroleum and petroleum residue and also the combination of the structure illustrated in the drawings Fig. 7 and 8, the appertaining hydraulic cleaner and the adaptation of the same for the above purpose.

In the drawing Fig. 1 represents a longitudinal section of the proposed construction of the retort; Fig. 2—a plan; Fig. 3—a section along the line *d-h* (Fig. 2) of the upper connecting section; Fig. 4—a section of the retort along the line *a-c* (Fig. 1); Fig. 5—a plan, and Fig. 6 a section along the line *f-c* (Fig. 5) of the lower connecting support. Fig. 7—a longitudinal section of the general arrangement of the retort and purifying apparatus; Fig. 8—a cross section of the cooler.

The proposed retort, in practice, consists of several (in the present case of 5) separate retorts, which in the general system represent chambers, and at the same time, being isolated from the other chamber retorts, may serve as independent retorts. All these retort chambers *n-n* are inserted with their lower ends vertically into depression circularly disposed in the upper cover common to all retorts of the cylindrical support B-B. At their lower end the depressions are covered by the covers 9 which serve [fol. 900] the purpose of closing the retorts.

In its middle the support has a through longitudinal opening (passage), so that the lateral outer and inner walls of this support form a complete annular space, divided by radial partitions, with windows in them, into as many parts as there are retort chambers, and the lower open end of each retort enters a separate section formed by two adjacent radial partitions. A similar addition A turned with its open end (i. e. with the covers) upward, is put on the upper ends of the retorts and fastens them together in vertical position. The windows *h* in the partitions are closed by thin cast iron slides (boards) which fit into slots and are sealed with clay. When thus assembled, the system of retorts represents a cylinder, having a through longitudinal passage inside, and when the longitudinal spaces between the retorts are closed with clay, the passage will be impervious on its sides and open at both ends. In this form, the compound retort is vertically installed and built into the furnace (Figure 7), which is laid out so that a free access passage to the covers of the retorts is left underneath. The furnace A is built to one side of the retort and the smoke turns (chimney gas passages) wind around the retort three times spirally, so that the flame reaching the upper part of the furnace turns through the movable arc shaped bend B′ into the passage of the retort, from the lower end of which the products of combustion are carried off into the smoke burning pipe L.

Assuming that all the windows (slides) in the lower support are open and that into each retort is admitted a separate stream of petroleum (erude oil), in such a case the compound retort will correspond in its action to five separate retorts of a single system. The gaseous products of the distillation from all the retorts will collect in the lower support, and through the common opening in it R′ may pass into the subsequent apparatus. In the same way it is possible, for instance, to operate (to work with) three retorts, and in the remaining two to superheat the oil vapors, for which purpose it is only necessary to open one of the partitions in the upper addition and close two partitions in the lower support, etc. Hence, according to requirements, it is possible to shorter or lengthen the path traversed by the oil vapors. To increase the heating surface of the retorts, almost the whole interior of each re-

tort is filled with massive iron chains the upper ends of which are attached to a common stem fastened to the upper [fol. 901] cover of the retort, and the lower ends hang freely, reaching to the windows in the partitions of the lower supports of the retorts. The stem of the chains passes through the cover outside, and is movable freely in the cover of the retort. The opening through which the stem passes serves at the same time for the installation of a device with a funnel, separating the interior of the retort from the atmospheric air and admitting the oil to the retort. The advantage obtained by the possibility of lengthening or shortening the path of the oil vapors at will, consists, according to the explanations of the petitioner, in obtaining a gas of uniform illuminating value independent of the density and the rate of inflow of the oil or of the constancy of temperature of the retorts. The lower and upper parts of the compound retort, which are covered with bricks, can not burn out, only the inner retorts may burn out; but in case one out of several of the latter is damaged, the compound retort may still work satisfactorily, if the damaged retort is isolated by closing the corresponding windows. In changing the burned out retorts, the furnace is not destroyed. It is only necessary to take off the upper addition and change the retort. The considerable clearances between the retorts insure the convenience of such an operation. In the upper as well as in the lower addition (headers) there is one outlet for the gas and both of these outlets are connected by a common pipe *g-g* into a single passage, leading to the hydraulic (washer), so that it is possible to utilize one of these or both of them by opening or closing the corresponding windows, as may be necessary in distributing the flow of the gases through the chamber retorts. On account of the mobility of the inner structure, the compound retort may operate almost continuously, since in order to clean it from incrustation, it is only necessary to stop the inflow of oil and make, by means of the stem, with the chain, several motions up and down, when through the rubbing of the chains between themselves and the walls of the retorts, the incrustation will drop, whence it can be removed through the lower cocers three to four times a month. The number of retorts composing a common retort may be increased or decreased with certain limits.

The hydraulic (washer) for three retorts (Fig. 7) consists of a vertical cylinder whose height is almost the same as its diameter, and whose volume corresponds to the quantity of gas flowing through it in a unit of time. (If 1 cubic foot of gas passes through in a second, the volume of the cylinder should be at least ten times greater, i. e., [fol. 902] 10 cubic feet). The pipes A carrying off the gas from the retort are immersed in water 1/2 to 3/4 inches; their ends pass under the bottom of an inverted cylindrical vessel O, resting with its open end on the bottom of the cylindrical hydraulic (washer). The height of the bell O represents about 1/3 of the height of the cylinder, and the diameter is 2-3 inches less; the bulged out bottom of the bell, has an opening in its middle, equal to the sum of the opening of the pipes admitting the gas; above is fastened another vessel O′ whose diameter equals 1/2 to 3/4 of the diameter of the bell O, the height of its walls 2 inches, and the bulged out bottom has a hole in the middle as in the bell O. At the very circumference of the upper vessel O′ through the bottom of both vessels is admitted a tube C, which, passing through the lower bottom of the hydraulic ends on the outside of the apparatus in an upwardly turned bend, approximately 1/2 the inner height of the tube, serving as a water seal (hydraulic closure). Above the vessels, O, O′, is installed an umbrella (hood), X-X, with a cut-out portion in its middle, and above it another hood, X′-X′, whose diameter is greater than the opening in the first hood. Above the hoods is fastened a screen upon which is placed coke in large lumps. The water, inflowing in a small stream through the tube M, falls upon the screen N′, spreads over it and moistens the coke in all directions, washing the solid and liquid particles which have settled upon it from the gas, and flowing down together with such particles, over the first and second hoods, X, X′, into the space *p*, *p*, between the walls of the "hydraulic" and the vessel O. The water is admitted into the apparatus in inconsiderable quantities, and besides, its increase is equal to its loss. Hence the water rising in the space *p*, *p*, will only begin to escape through tube C, when the whole supply of water originally contained in the apparatus is exhausted. By that time the water, not being disturbed, neither in the space, nor in the lower layers, will have time

to settle, so that the heavier particles washed off the coke settle at the bottom and the lighter ones on the surface while the clean water passes gradually through the windows (openings *v*, *v*, in the walls of the vessel, into the inside of it, forcing out the upper layers of the liquid heated by the gas penetrating through it, and containing heavy grease, so that these layers of the hot greasy water are gradually poured out through the central openings in the vessels O, O′, and are partly thrown off by the gases entering through the same aperture, towards the opening [fol. 903] in the tube C. At the same time, clear water constantly flows in, replacing the hot liquid, which water has cooled the upper parts of the apparatus and has settled in its lower parts.

The light grease floating on the surface of the water between the walls of the "hydraulic (washer) and the vessel O, as it accumulates, passes through the edge of the upper vessel O′, and goes out through the same tube C, and the heavy tar falls to the bottom of the washer and is periodically drawn off through the valve *d*. The gas entering under pressure, which it has in the retort, through the tube A, passes through the water to the opening in the bell O, O in the form of bubbles, assisting the throwing off of the upper hot and dirty layers of liquid into the vessel O′ O′ and tube C. The washed gas passes around the hoods and is spread out in the coke, whence partly cooled, and leaving in the layer of coke, the undecomposed particles of oil and coal which it had carried away mechanically, it starts along the pipes A, A, towards the cooler.

The cooler consists of a vertical cylinder whose height is at least 4 or 5 times greater than its diameter, and whose volume is not less than the volume of the washer. This cylinder is completely filled with iron chips. The gas entering through the pipe A^3, below, scatters between the iron chips which are cooled with water. In its rise to the top, it meets continuously colder layers of chips, and finally passes out through the pipe, A^4 at the top of the cooler. The water, admitted at the top, cools the chips and at the same time prevents clogging of the apparatus, carrying away towards the bottom the solid and liquid particles which have settled out of the gas, so that the upper layers of the chips, located near the outlet of the gas are always

clean. The tarry remnants and the warm water pass out of the apparatus through the pipe *d'*.

The cleaner (scrubber) has the form of a box and is made of wood. A frame T, T, is built of wide boards open on both sides with a transverse partition A, to which, as well as to the opposite wall inside the frame, is fastened the washing apparatus proper. The latter consists of a wedge shaped board *y*, lined underneath with sheet iron, with combs (baffles) *g' g'*, rivited on to it. Upon the edges of the wedge *y* are placed wooden planks, *s, s,* (Fig. 8) covered thorughout their length with sheet iron (whose width is 2-1/2 to 3 times greater than the width of the wedge), [fol. 904] so that the equal sides of the street are bent along the edges of the edges and hang down not less than 2-3 vershock (Russian measure of length, about 1-3/4″). At the thicker end of the wedge in the upper part of this sheet is made a cut (aperture) equal in width, to the distance between the planks, and in length, not over 1/2 arshin (1 arshin equals 28″). All this is fastened together and is installed along the frame on the inside (as shown in the drawing). Then the screen M^2 is fastened on, and the frame is sealed hermetically at both ends with iron *v. v.* In the upper board of the frame there is a manhole through which coke, hay or a cleaning mixture (Laming's or another) is placed in the upper compartment of the cleaner; into the lower compartment, water, milk of lime, or another liquid is admitted. The level of the liquid will never be higher than the window Z. Gas enters from the cooler along the pipe A^4, into the compartment, S, through the window R, and, forcing out the liquid, passes under the wedge through the baffles *g', g',* being divided by the latter into fine bubbles. Reaching the end of the wedge, the gas turns into the passage W formed between the wedge and the upper sheet, and drives before it the liquid forced out from under the wedge, which runs downwards along the wedge, meeting a new stream of gas, which splits it up into little streams and is split up and washed in its turn. The gas after having thus been washed, enters through the screen M^3 into the upper compartment (scrubber), where in passing in a long path over porous substances, it is freed from water vapors, and, if necessary, also from other injurious admixture, and then it is carried off along the pipe A^5 into the gas holder.

The residues from the distillation of all the apparatuses is carried off, mixed with water, through the conduit N, N, into the first compartment of the sediment box K, K, from which the water is removed through the valve *v* into the waste pipe M, M in a constant stream almost equal to its inflow to all the apparatuses, and the lighter by-products (remnants of the distillation), flow slowly into the second compartment of the sediment box. Here these by-products settle and almost in clear form pass through the valve 6 ino the reservoir P, whence they are removed or pumped out periodically. The heavier tarry remnants are carried away from the first compartment of the box into the second along the incline N^2 through a window in the partition 1 and are then also discharged through the valve 6 into the reservoir P, whence they are removed as they ac- [fol. 905] cumulate. The water settled off the residue is discharged from the receiver P by means of a valve g^2 into the cesspool, *u*, *u*.

The advantages of the cleaners, described consist, according to the statement of the petitioner, in the possibility of attaining the proper purification of the gas without the aid of an exhauster.

In Figures 1 and 10 is illustrated an assembled retort with a device for the uniform distribution of oil over the whole heating surface, installed in the surface. The group consists of 5 separate vertical retorts or chambers *n*, *n*, whose upper and lower ends enter into the upper and lower baskets (Headers) *a*, *a*, for which purposes both headers have nests with flanges corresponding to the form of the retorts. Into these nests, disposed around the circumference of the headers, are inserted and sealed with refractory material the ends of the retorts *n*, *n*. Inside the headers in the spaces between the nests, there are radial partitions with windows, *h*, *h*, which are closed by cast iron slides entering into slots on the sealing material. In such a manner, by means of the headers, the separate retort chambers are combined into one common assembled retort; at the same time these chambers are made to communicate, or are separated, as required, by means of the aforesaid windows, *h*, *h*. If in the upper header all the windows, *h*, *h*, were closed and those in the lower one open, and into each retort chamber a separate stream of oil is admitted,

the action of the group will correspond to the action of five separate retorts, with the difference, that the gaseous products from all the chambers collect in the lower header, whence they pass to the condensers through the common pipe C. But if it should be necessary to obtain tar having a certain quality, as explained below, it is possible to operate 2, 3 and even 4 retorts and in the remaining ones only superheat the mixture of gases obtained from the first ones. Thus, for instance, closing all the windows in the upper header and leaving them open in the lower one, it is possible to work 4 chambers, and to pass the gases thus obtained in the lower header upwards along the fifth chamber, and to direct them through the outlet pipe C′ into the common condenser. In the same way, closing 2 windows in each of the upper and lower headers, it is possible to operate 3 retorts, and in the remainder to superheat the gases.

The retorts with a constant heating surface (Fig. 11 and 12) differ from those previously described only by the fact that they have no headers with windows as referred to [fol. 906] above, but are connected into a common group by installing them upon a common gas receiving header W, while the upper ends of the retort are held together by a common flange *w*. All the rest, such as the inner structure, the system of heating, etc., remains as before. The retorts of either systems are installed in groups of two, three, four, five or more separate retorts, as may be most convenient in heating the forms, but they may be installed separately. In a word, the quantity (number) and form of cross section of the retorts may be varied in accordance with the dimensions of the plant constructed, but the system of heating and inner structure is always the same.

Several of these modifications are illustrated in Figures 9-15 of the drawing. The inner construction of the retorts of the proposed system is adapted exclusively to operate with liquid materials. For this purpose, each retort is provided with a distributing device (Figs. 16 and 17) which is installed in the upper part of the retort and consists (a) of a cast iron reservoir K; (b) a cylindrical basket (header) *x*, *x*, with fine openings *v*, *v*, disposed around its outer wall, and (c) a cast iron hood *b* with as many radial channels (veins) *b′*, *b′*, as there are openings in the header

x. The purpose of these veins is to direct the liquid towards all the points of the circumference of the retorts. The device is fed from the funnel M, installed outside on the cover of the retort. The liquid enters along the pipe M into the reservoir K, serving as a hydraulic seal for the gas and a preheater for the liquid. The cold liquid admitted to the reservoir K from below replaces the liquid, which has entered there previously and already preheated, through the upper openings g, g, into the compartment f. Thence the liquid goes through the horizontal row of the above mentioned openings, v, v, onto the teeth, v, v, whence they are broken off in drops and fall downward parallel to the highly heated walls of the retort, and very close to them. At the same time each separate drop, preheated in the distributing apparatus absorbs heat not from some particular point of the heating surface of the retort, but from all points, past which is has to travel. According to the explanation of the petitioner, the rise of temperature of the falling drop is accomplished so rapidly, that this drop does not have any time to boil out gradually (to evaporate slowly), but, on the contrary, is decomposed at once into its constituent hydrogen parts; in other words, the drop receives so much heat in a brief time, that this heat is suffi- [fol. 907] cient to simultaneously turn the heavy and light hydrocarbons into a gaseous state. Of course, no matter how short the time during which the drop is heated, still it has a certain magnitude, consequently, strictly speaking, in accordance with the gradual rise of temperature, the evaporation of the drop will also take place gradually. But the time necessary for the destruction of the drop is actually almost instan-eous; although the periods of rise of temperature do exist, they are so short, that the different kinds of liquid forming the drop begin to boil almost at the same time. The gases formed strive to separate and, by their instantly developed elasticity break the non-evaporated remainder of the drop into particles, which in their turn are subjected to the same treatment (suffer the same fate), but still more rapidly and thoroughly, for the reason that being smaller they are heated more conveniently. As a result, if at a certain depth of the retort there are still minute liquid remnants, they may reach there only in very fine form, and therefore, in view of their negligible

weight will drop slowly, thoroughly dividing the movement of the gaseous particles.

In order to increase the heating surface of the retort for the purpose of uniformly heating, and mainly, for the complete intermingling of the gaseous particles among themselves as well as with the above mentioned pulverized liquid particles, a device is constructed consisting of cast iron balls *p, p* (Figs. 9, 10, and 11) connected by chains to one another and to the bar *p'* which its head p^2 is attached to the distributing apparatus (Fig. 16). Should the bar be turned 90° above its axis, its head will get off the shoulders *f, f,* and pass freely downward through the cutouts f^2, f^2, in which case the bar with the hollow balls will, of course, also come down. On the inside, the walls of the retort are provided with several vein-like furrows, running the whole length of the retort in the form of a spiral out (rifling) from 3 to 4 turns. Thanks to the ball *p.* the cross section of the inner space of the retort is narrowed down at several places. Hence the vapors moving past them towards the outlet, are contracted and are subjected to closer contact with the highly heated walls of the retort. Passing the ball, the gases expand again until reaching the next one—expands again, and so on. Each time in the narrowed passage, especially upon rise in temperature, the velocity of movement of the vapors is increased, hence these vapors starting along the spiral furrows of the retort, not only are themsedves set into rotation, but carry with them the pulverized liquid substances along the curve [fol. 908] of their own movement. In this manner, all the various gases and the liquid particles, moving spirally and passing a narrowed place, collide, come in contact, and constantly change their relative position, i. e., they are completely intermixed. By the complete mixture and heating of the various kinds of vapor particles, all the favorable conditions for stimulating chemical reaction are produced, according to the explanation of the petitioner. But if in the lower part of the rectort there will still remain some pulverized liquid particles, then, thanks to the state of the whole mass at the moment of its decomposition, when its elements tend to form new chemical combinations with the greatest energy—these particles will react strongly with the vapor particles and form new vaporlike combinations.

In order to lengthen the path, and consequently also the time of heating and the process of chemical reaction of the various particles, the above described spiral path is imparted to them, being longer than the straight path and slowing down the time of movement.

As a result of this slowed down chemical reaction, there is obtained a tar containing aromatic hydrocarbon, of which they there are almost none in the crude oil in its ready form; they are formed by the decomposition of the oil from the aggregate of new chemical combinations, hence, the more perfect the decomposition and the more complete the chemical reaction, the higher the quality of the tar. The illuminating gas will be obtained at the same time without an excess of oil forming gas, which produces soot upon burning and condensation in the pipes. Besides this, due to the conversion of almost the whole material into vaporized state, no incrustation is formed in the retort, by which means the defect present in horizontal retorts, resulting in non-productive loss of time for cleaning the retorts, is avoided.

Although there is no coke forming or asphalt incrustation in the retort, there is formed a very fine dust (microscopic particles of carbon) settling inside on the walls of the retort in the form of down, which, dur to their insignificant weight, are immaterial as to the loss of material, but (settling on the walls) lower the heat transmitting quality of the retort. Hence in case of continuous running, it is necessary to clean off this layer once or twice in 24 hours. For this purpose the stopper *y* (Fig. 12) is screwed out of the cover of the retort. Through the opening thus formed the reservoir K is taken out and upon the thread of the bar *y'* a stem is screwed on, by means of which the [fol. 909] balls and chains are raised and lowered, and the soot is knocked off. For a more thorough cleaning, wire disks in the form of brushes are placed on the chains.

Upon the expiration of several days of continuous run, for the complete cleaning of the retort from particles adhering more firmly to its walls, the retort is blown through and burned out. For this purpose, both the lower and upper covers are opened. The air entering from below forms a strong draft, igniting the gas remaining in the retort, and all the particles which have settled on the walls burn out

clean. Such a cleaning takes no more than ½ an hour's time, after which the run may be renewed at once, since during the above described cleaning the fire in the furnace is not stopped. The separate retorts, assembled in the above manner into one common retort, are installed vertically and heated by the travel of the flame, which starting from below winds spirally around the outer walls of the common group of retorts upward, thence it enters into the space between the retorts, heats the retorts throughout their length and finally turns downward into the smoke chamber L, of the factory chimney.

The construction of the furnace is shown in Figures 9 and 10. The groups of retorts are installed so that under the furnace there should be a free access to the lower covers or to the common hole through the lower header *n*, and in case of a single retort to the outlet pipe. In order that the outer spiral passage should not communicate with the one between the retort, the small spaces 1, 1, between the retorts are closed from top to bottom (as shown in the drawing) with pieces of refractory brick, according to the size and form of such spaces, and the big space serving to connect the outer passage with the space between the retorts, is closed with brick only in its middle part, while above and below corresponding spaces 1′, 1′, are left. The structure of the furnace for the assembled 5 chambered retort only is shown on the drawing, since for all others, the furnace is the same. In such cases when the retorts are intended only for obtaining illuminating gas and it is proposed to run them continuously, the furnace is built in reverse order, i. e., the flame is admitted first into the space between the retorts from below, upwards, thence it is directed downwards along the spiral turn from above.

Fig. 18 of the drawing represents partly a front view of the furnace and partly a vertical section of a modified construction of the retorts with a generator. Fig. 2 is a plan on a horizontal section. The modification consists here of [fol. 910] the screw from insertions R, R. The annular space of the retort contained between the walls of the latter and the pipe A is divided by the insertion (core) R, R, into several compartments or chambers which communicate by means of the spiral passages, cut in the surface of these insertions. The latter have right hand and left hand spiral passages alternately, as shown on the drawing. The above

mentioned chambers take the place of the chamber retorts in the apparatus of the previous construction and in their action are identical with them. The only difference consists in the fact that these chambers are placed in one retort, so that each retort represents a compound retort, consisting of several separate chamber retorts. The action of the insertion R, R, consists in that the gases formed in the upper part of the retort and the remaining non-evaporated pulverized liquid particles, circulating downward and passing through the spiral passages from one compartment to the other, are intermixed, uniformly heated and undergo final decomposition. The products of the decomposition rise along the pipe K upwards into a compartment disposed above the distributor, thence into the hydraulic H and further. The heating of the gas in the present case is brought forth by the use of producer gas, supplied to the furnace through the pipe B. But in the furnaces of such a construction, it is also possible to use heating by liquid oil supplied by means of a force nozzle (spray nozzle). The flame and the highly heated products of combustion, rise upwards between the retorts, while the hotter gaseous particles circulate in the upper space of the furnace, and those particles which gave up their heat, i. e., worked out, being colded and heavier; drop downward and through the channels (windows) *h*, *h*, pass into the upper space G, whence they are directed to the check valve M into the right or left regenerator.

In Figs. 18 and 19 is shown one such generator in vertical and horizontal sections. At the same time and by the same check valve M the superheated air is admitted from the second regenerator into a second annular space disposed below, whence it passes by the channels *h*, *h*, into the furnace. The check valve N, on the other hand, admits the exhausted products of combustion from one generator into the smoke stack, and at the same time admits cold air by preheating into the other regenerator. Both of these check valves are interconnected by a system of levers and are brought into action by means of one handle P. The direction of movement of the used up products of combustion and preheated air is indicated on the drawing by the arrows.

[fol. 911]

PETITIONER'S EXHIBIT 121

No. 659,076. Patented Oct. 2, 1900.

F. LENNARD.

PROCESS OF SEPARATING FREE CARBON FROM TAR.

(Application filed Aug. 20, 1900.)

(No Model.) 2 Sheets—Sheet 1.

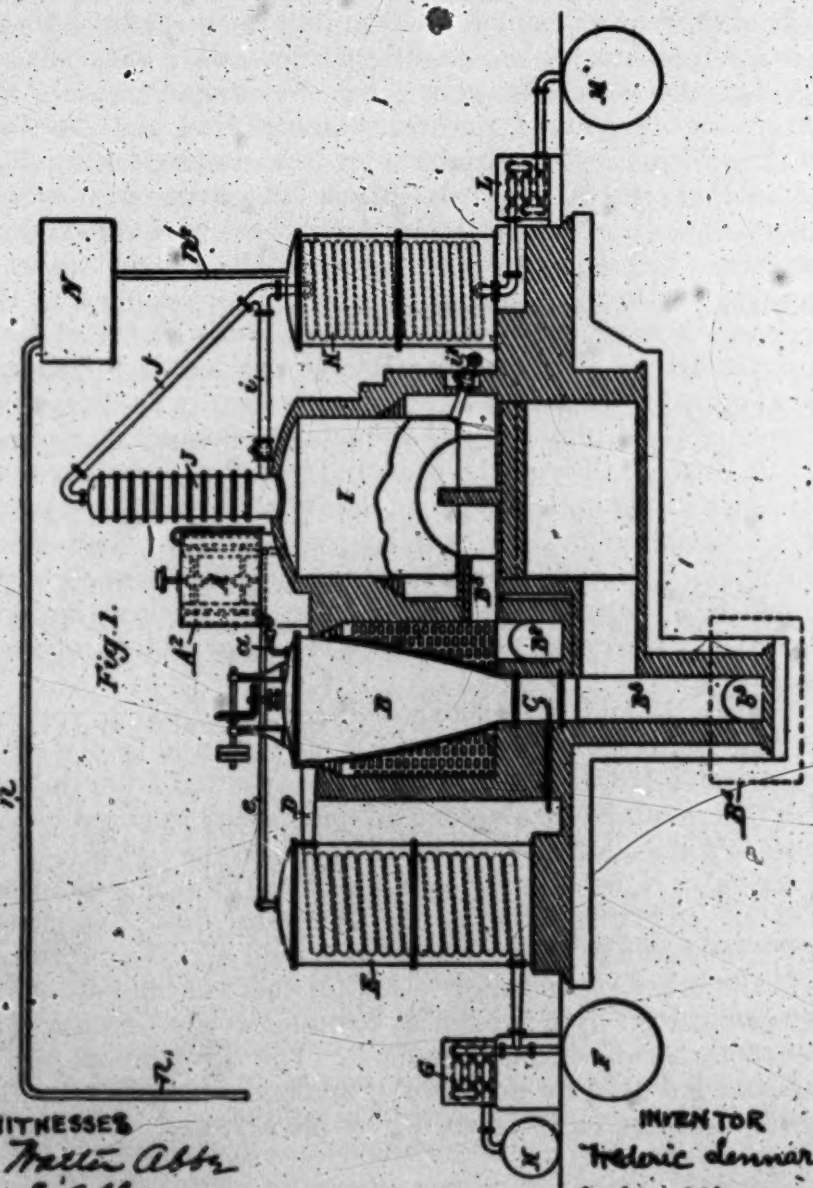


Fig. 1.

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[fol. 912]

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PROCESS OF SEPARATING FREE CARBON FROM TAR.

(Application filed Aug. 22, 1899.)

(No Model.) 3 Sheets—Sheet 2.

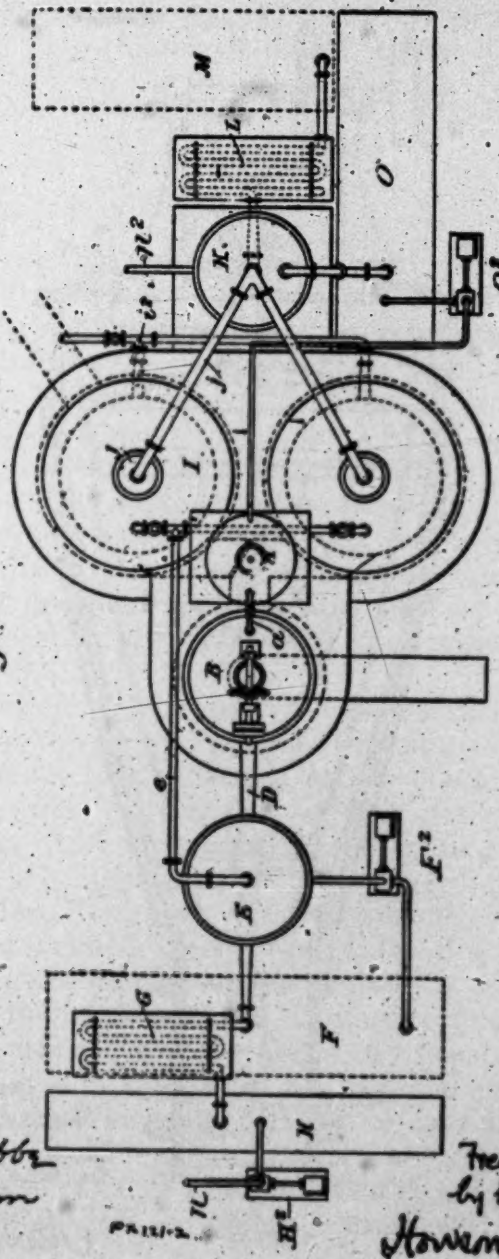

Fig 3

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[fol. 913]

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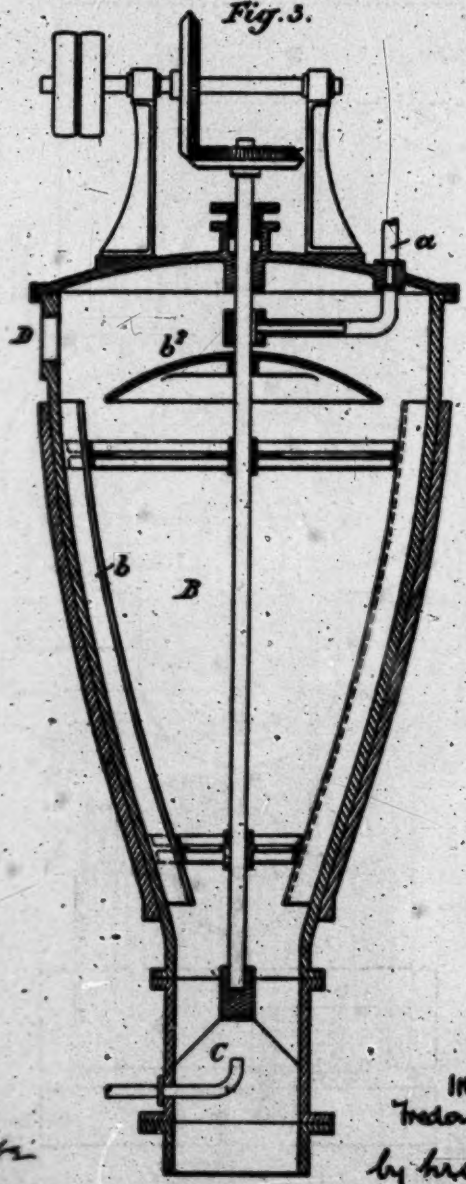
PROCESS OF SEPARATING FREE CARBON FROM TAR.

(Application filed Aug. 28, 1899.)

(No Model.) 3 Sheets—Sheet 3.

Fig. 3.



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Process of Separating Free Carbon from Tar

Specification Forming Part of Letters Patent No. 659,076, Dated October 2, 1900

Application Filed August 22, 1899. Serial No. 728,096 (No specimens)

To all whom it may concern:

Be it known that I, Frederic Lennard, chemical manufacturer, a subject of the Queen of Great Britain and Ireland, and a resident of 70 Gracechurch street, in the city of London, England, have invented certain new and useful Improvements in the Process for Separation of Free Carbon from Tar, (for which I have applied for a patent in Great Britain, No. 2, 183, date January 31, 1899,) which invention is fully set forth in the following specification.

Tar, and especially coal-gas tar, contains free carbon, which retards the distillation of the tar, causes undue wear and tear of the distilling apparatus, and reduces the value for agglomerating purposes of the pitch produced from distillation of the tar.

My invention has for its object to separate the free carbon from the tar, so as to increase the value of the pitch produced when the tar is distilled and to obtain the said free carbon in a valuable form for electrical and other purposes.

According to my invention I dilute the tar from which the carbon is to be separated with naphtha, light oil, or any other suitable oil or spirit of low specific gravity to such an extent as to diminish the viscous nature of the tar and produce a mixture having an appreciably-lower vaporizing-point than the tar alone has. Having so diluted the tar, I pass the mixture into a chamber or retort externally heated to the volatilizing-point of the mixture and subject it to the action of steam, which has the effect of depriving it of practically all its liquid portion, the free carbon being deposited in the form of a rough powder. The chamber or retort in which the mixture is so treated is preferably of somewhat-

conical-form, smaller at bottom than at top, and is provided with a rotating scraper and with a spreader at top to distribute the mixture of tar and light oil or spirit, the steam being admitted by a jet or jets projecting upward from the lower part of the chamber or retort, the bottom of which is provided with a seal, which may be constituted, for example, by a water-well or an air-tight receptacle, into which the carbon falls and from which it can be removed at intervals.

The volatile products driven off from the mixture can be condensed, the lighter oil or spirit being recovered for reuse and the remainder being conducted (if desired, through an interchanger through which the aforesaid volatile products pass) to a still, which can be heated by the otherwise waste heat from the aforesaid chamber or retort. The tar to be treated can be preheated, if desired, by passing it through an interchanger through which the products of distillation pass from the still.

The accompanying drawings represent apparatus suitable for the purposes of my invention.

Figure 1 is a sectional elevation, Fig. 2 a plan, and Fig. 3 an enlarged section, of the chamber or retort B.

The mixture of tar and oil or spirit of low specific gravity, preferably previously heated, as hereinafter described, is supplied from a tank A (provided with an agitator A^2) by the pipe *a* to the chamber or retort B, heated by the furnace B^2 and provided with a rotating scraper *b* and with a spreader b^2.

C is a pipe and jet by which steam is admitted and projected upward from the lower part of the chamber or retort B, the bottom of which is provided either with a water-well B^3 constituting a seal into which the carbon falls and from which it can be removed as required by the outlet b^3, as shown in full lines in Fig. 1, or with an air-tight receptacle B^4, as shown in dotted lines in that figure. The volatile products driven off from the chamber or retort B pass off by the pipe D and through the coil of the interchanger and condenser E, from which the condensed portion passes into the receiver F, the uncondensed portion passing through the coil in the auxiliary condenser G and thence into the receiver H, from which it is pumped by the pump H^2 through the pipe *n* into the mixing-tank N for mixing therein with a further quantity of tar. The condensed products from the receiver F are pumped by the pump F^2 around the outside of the coil

in the interchanger and condenser E, so that they may serve as the condensing medium of the products from the chamber or retort B, which, as aforesaid, pass through the said coil, the said condensed products then passing by the pipe *e* to a still I, which can be heated by the hot products of combus- [fol. 915] tion from the furnace B^2, which heats the chamber or retort B, the said products passing through the flue or passage B^5. The first or lighter products of distillation from this still I are passed through the fractioning-column J and by the pipe *j* through the coil in the interchanger and condenser K and thence through the auxiliary condenser L into the receiver M or receivers. The heavier or last portions of distillation from the still I afterwards pass through the pipe *i* and interchanger and condenser K and auxiliary condenser L into receiver or receivers therefor. The residue left in the still is withdrawn by the outlet i^2 for use or for further treatment, if required. I preferably employ the mixture of tar and oil or spirit as the condensing medium for the interchanger and condenser K, so that the said mixture may be heated before being introduced into the retort. This mixture passes from the tank N into the interchanger and condenser K by way of the pipe n^2, and after flowing around the outside of the coil of such interchanger and condenser it overflows into a vessel O, from which it is pumped by the pump O^2 into the tank A, which, as previously described, supplies the retort B.

If desired, instead of the mixture of tar and oil or spirit being used as the condensing medium in the vessels K and E, as previously described, water or other condensing agent may be employed for the purpose, though I prefer the former arrangement, because while the said mixture serves as the condensing agent it at the same time becomes heated preparatory to its treatment in the retort B and still I.

Without intending to limit myself thereto, but by way of example only, I will state that the following detailed procedure may be employed in carrying out my invention: One thousand gallons of crude coal-tar are mixed with an equal quantity of coal-tar naphtha of about from 860° to 950° specific gravity, and the mixture is kept thoroughly agitated. This mixture after being slightly warmed by a steam-coil is then fed in a small stream into the retort hereinbefore described (which has been heated to a temperature of 500° centigrade) and falls onto the heated sides of the said re-

tort, which causes volatilization of the liquid portion, the free carbon adhering to the walls of the retort and being removed by the revolving scraper, so that it falls into the air-tight chamber, from which it is taken from time to time.

I claim as my invention—

The process of distilling tar to separate the free carbon therefrom, consisting in diluting the tar with an oil or spirit which will, in combination with the said tar, produce a mixture having an appreciably-lower vaporizing-point than the tar alone has, and subjecting the mixture to the action of heat and of steam, and thereby effecting simultaneously the volatilization of the liquid portion and the deposit of the free carbon, substantially as described.

In testimony whereof I have signed this specification in the presence of two subscribing witnesses.

F. Lennard.

Witnesses: William Frederick Upton, John Edward Newton.

[fol. 916]

PETITIONER'S EXHIBIT 122

R. F. BACON, B. T. BROOKS & C. W. CLARK.

MANUFACTURE OF GASOLENE.

APPLICATION FILED MAY 2, 1913.

1,131,309. Patented Mar. 9, 1915.

Fig. 1.

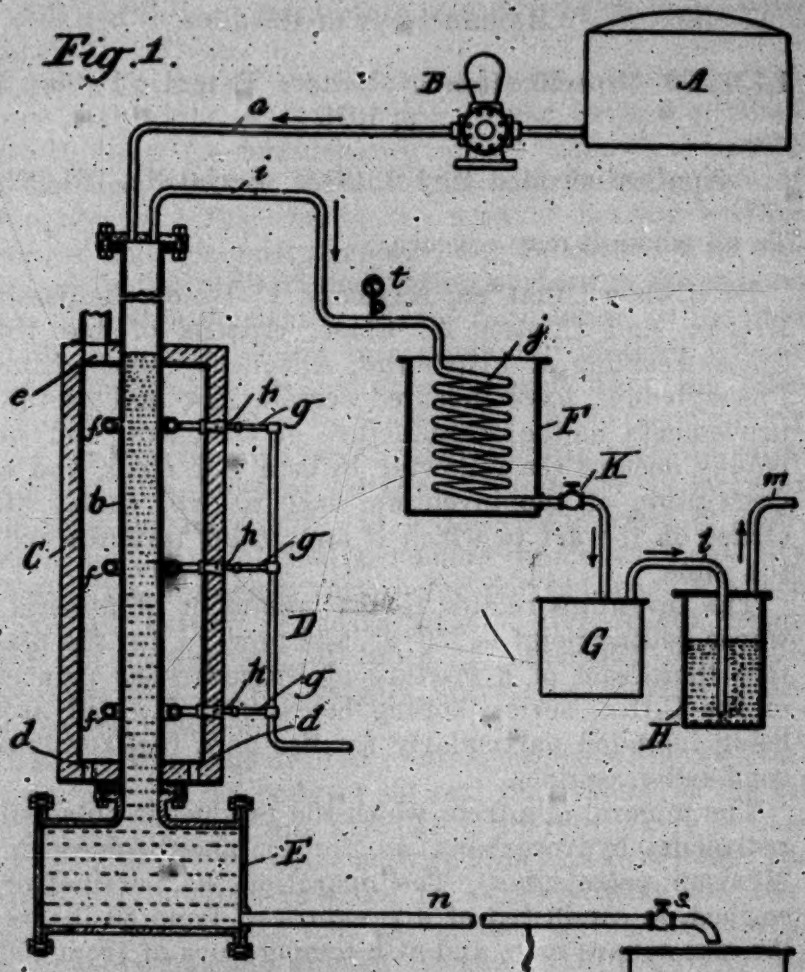
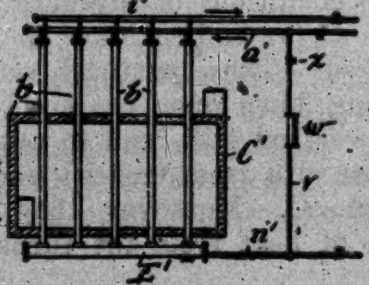


Fig. 2.



WITNESSES:
W. A. Bill
H. Lindsley

INVENTORS
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Benjamin T. Brooks,
Clinton W. Clark.
Curtis, Davis & Goldsborough
ATTORNEYS.

[fol. 917] United States Patent Office

Raymond F. Bacon, Benjamin T. Brooks, and Clinton W. Clark, of Pittsburgh, Pennsylvania, Assignors to Gulf Refining Company of Pittsburgh, Pennsylvania, a Corporation of Texas.

Manufacturer of Gasoline

1,131,309. Specification of Letters Patent. Patent Mar. 9, 1915

Application filed May 2, 1913. Serial No. 764,982

To all whom it may concern:

Be it known that we, Raymond F. Bacon, Benjamin T. Brooks, and Clinton W. Clark, citizens of the United States residing at Pittsburgh, Allegheny county, State of Pennsylvania, have invented certain new and useful Improvements in the Manufacture of Gasolene; and we do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

The invention relates to the treatment of mineral oils whose boiling point is 250° C. and upward, for the production therefrom of a mixture of hydrocarbons principally of the C_nH_{2n+2} series, boiling below 200° C., said product being intended particularly for use as a fuel for internal combustion engines.

The mineral oils from which the product is obtained are petroleum hydrocarbons, as, for instance, American and Mexican petroleums. The operation, as hereinafter described, is conducted at a pressure of from 60 lbs. to 300 lbs. per square inch, and at a temperature of from 350° C. to 500° C. Under these conditions of pressure and temperature, small particles of tar and coke are continuously produced in the body of oil. These particles, settling out of the mass and dropping down upon the hot bottom of the usual horizontal or vertical still tend to agglomerate and adhere to said bottom with great tenacity and are difficult of subsequent removal. Moreover, they not only diminish the conduction of heat from the furnace gases

to the oil within the still, but it is found that they increase the danger of explosion by increasing the tendency of the still bottom to burn through.

The present invention is designed to avoid the difficulty just referred to, by conducting the operation under such condition that the particles of tar and coke produced in the mass will tend to move out of the cracking zone of the still and deposit themselves in a part of the apparatus separate therefrom.

Another feature of the invention is based upon the discovery that while the production of the desired product depends upon the maintenance of the high temperature and the high pressure hereinbefore described, the rate of production is a function of the area of heating surface employed and, for most purposes, may be regarded as represented by the ratio of the heating surface to the volume of the oil within the heating space. Accordingly, it is found that the maximum yields, in a given unit of time, from a given volume of oil heated, are obtained when the ratio of the heating surface to the volume is correspondingly large. In practice, we have employed with entirely satisfactory results, tubes of an internal diameter as large as 19 inches (corresponding to a ratio expressed in comparable units, of internal periphery to internal capacity of 1:47; this numerical ratio being derived when the inch is taken as the unit of measurement). We do not recommend the employment of tubes of materially larger diameter because of the rapidly decreasing yield in gasolene beyond that point.

In establishing the desired relationship between the heating surface for the body of oil and the volume of the oil undergoing cracking and distillation thereby, there is likewise embodied in the same construction and procedure, the feature hereinbefore referred to, of permitting the particles of tar and coke that are formed during the operation to move out and deposit themselves in a part of the apparatus separate from the heated surfaces which effect the cracking of the oil. Thus, in the preferred practice of the invention, the still is constructed in such a manner that its heating zone is upright and is a portion of a tube, of small diameter with respect to its length. The tube is supplied with the oil in any suitable manner, as, for instance, by a pump discharging into its upper portion. At

its lower end, the tube leads into a receptacle for the collection of the tar and coke particles. The arrangement is preferably such that the receptacle in which the tar and coke are received is entirely below the heating zone of the tube, so that the particles of tar and coke will fall freely through the oil column into the collecting space below in substantially their entirety. Whatever particles of tar and coke chance to be deposited upon the upright walls of the heating zone, their amount is relatively small, so that the clearing of the tube to remove such accretions is not frequently required.

It is further charactertistic of the present invention that [fol. 918] the danger of explosions is materially lessened and, in fact, is rendered almost impossible, at the pressures employed, because of the much larger resistivity to pressure incident to the employment of small tubes as compared with the employment of a single large still, either of the horizontal or vertical type.

In the accompanying drawing, Figure 1 represents, partly in section, and partly in elevation, a form of apparatus suitable for the practice of the invention; Fig. 2 represents a partial view of another modification of the invention, showing its applicability to advantage in multiple units.

Similar letters of reference indicate similar parts in both the views.

Referring particularly to Fig. 1, A indicates a storage tank for the petroleum hydrocarbons to be treated, and B indicates a pump for delivering a regulated supply therefrom to the still through the conduit *a*.

In Fig. 1, is shown a single unit consisting of a tube *b*, of steel or other suitable metal and whose length is preferably 20 ft. or more, when the internal diameter of the tube is 6 inches. The heating zone of the tube is intermediate of its ends and in the form shown in Fig. 1 consists of a fire brick chamber C having suitable air inlets, as *d*, and a suitable exit opening, as *e*, for the products of combustion. The chamber C may receive its heat from any convenient source, as, for instance, a series of annular gas burners *f*, supplied with a mixture of air and gas from the gas conduit D whose branches *g* terminate in injecting tips, as shown, and which draw in with them a suitable supply of air through the bell *h* opening into

the atmosphere. At its lower end, the tube *b* communicates with a tar and coke receiving receptacle E, located below, outside of the heating zone.

At the beginning of the operation, the charge of oil to be cracked and distilled is established up to the level indicated in Fig. 1, that is to say, at a level slightly higher than the internal wall of the top of the heating chamber C. This level of the body of oil is kept practically constant, by means of the pump B, which supplies oil to the interior of the tube as the cracking and distillation proceed. Accordingly, the products of combustion do not come into direct contact with any portions of the tube not occupied by the liquid oil, and consequently, the danger di[illegible]ation of any portion of the vapors by coming into contact with overheated portions of the tube above the zone of liquid oil is minimized and the formation of an adhering layer of coke upon such portion of the walls of the tube is voided.

The free portion of the tube extends above the furnace setting, as shown, for a distance of say 5 feet. The vapors pass, by means of the pipe *i*, to the condenser coil J, contained within the cooling receptacle F. The condenser coil is provided at its end with a valve *k* and discharges into the receptacle G. The uncondensed gases and vapors from the receptacle G pass by the pipe *l* into a body of oil contained within the receptacle H, wherein such particles of oil as are contained in the residual gases are trapped and recovered. The surplus gases and vapors pass off through the conduit *m*. At the bottom of the receptacle E, a pipe *n* conveys the residual tar and coke to a receiving tank I, the flow being under the control of a regulable valve *s*.

From the foregoing description of the purposes of the invention, and of the construction of the apparatus shown in Fig. 1, the mode of operation will be fully apparent. The receptacle E and the tube B, are filled to the level indicated, and the annular burners *f* are ignited. The temperature rises to the range hereinbefore referred to, that is to say 350° C to 500° C., and the pressure is likewise permitted to rise, by shutting off the valve K either wholly or partially, as the case may be, until the pressure gage *t* indicates the pressure desired, that is to say, a pressure within the range of 60 lbs. to 300 lbs. per square

inch. Thus, at 100 lbs. pressure, about 75-90% of the entire body of oil may be distilled with the production of a resultant condensate containing a large percentage of material boiling below 200° C., the temperature being about 425° C. About 35% of the condensate obtained at this pressure and temperature has a boiling point below 150°, and almost all of this product is of the C_nH_{2n+2} series, appropriate for use for the ordinary purposes of gasolene, as, for instance for use as fuel for internal combustion engines and would usually be rated commercially as gasolene. In general, it is preferred, as indicated, to operate at a pressure of 100 lbs. for the reason that the relative portion of material boiling below 150° C. is greater when the operation is conducted at 100 lbs. pressure than when conducted at the lower pressure of 60 lbs. per square inch. The higher pressures up to 300 lbs. are employed when it is desired to still further increase the relative proportion of material in the condensate boiling below 150° C., but at the higher pressures there is progressively more coke and gas formed and hence a lower percentage of total condensate is obtained.

During the cracking and distilling operation, any particles of tar and coke that may be formed in the body of the distilling oil tend to fall through the vertical heating zone, by gravity, into the receiving space of the chamber [fol. 919] E. A relatively small amount of tar and coke will, in the course of time, build up upon the vertical walls of the tube B within the heating zone, but these accumulations are relatively unimportant and slow of formation, and, should they become excessive, may be readily removed by the use of any ordinary boiler flue cleaner, or the like. The petroleum residue containing the coke accumulating in the receptacle E is drawn off from time to time through the pipe *n* into the receiver I.

In the form of the invention indicated in Fig. 2, there is shown a series of individual tubes *b*, having at the bottom a common header E′ corresponding in function and location to the receptacle E of Fig. 1. The tubes *b* are located in a heating flue C′ supplied with a flow of hot products of combustion from any suitable source, so as to heat the tubes to the high temperatures hereinbefore referred to, the header E′ being located in a cooler space below the heating flue. *g′* indicates a supply pipe communicat-

ing with the interior of the several tubes *b*, so as to furnish oil thereto. So also, the pipe *i'* constitutes the exit pipe for the vapors. The supply pipe *a'* and the exit pipe *n'* from the header E' are connected by the cross-connecting pipe *v* having a valve *x* and containing the liquid level gage *w*, so that the operator will be able to know at any time the oil level within the several tubes *b*. The mode of operation of this modification will be clear from what has been said in regard to the mode of operation of the form of the apparatus shown in Fig. 1, and need not be further elaborated.

Having thus described the invention, what is claimed is:

1. The method of producing from petroleum oils which have a boiling point of 250° C. and upward, a mixture of hydrocarbons boiling below 200° C., which consists in subjecting the petroleum oils treated to a combined cracking and distilling operation at a temperature within the range of 350° C. to 500° C., and at a pressure within the range of 60 lbs. to 300 lbs. per square inch, progressively removing from the heating zone the particles of tar and coke produced therein and depositing them out of contact with the walls of said heating zone; substantially as described.

2. The method of producing from petroleum oils which have a boiling point of 250° C. and upward, a mixture of hydrocarbons boiling below 200° C., which consists in subjecting an upright column of the oil to a combined cracking and distilling operation at a temperature within the range of 350° C. to 500° C. and at a pressure within the range of 60 lbs. to 300 lbs. per square inch, and permitting particles of tar and coke produced in the upright column of oil to fall by gravity from the upright column into a receiving space below said column; substantially as described.

3. The method of producing from petroleum oils which have a boiling point of 250° C. and upward, a mixture of hydrocarbons boiling below 200° C., which consists in subjecting the petroleum oils treated to a combined cracking and distilling operation at a temperature within the range of 60 lbs. to 300 lbs. per square inch, and establishing during the cracking and distilling operation, a ratio (expressed in comparable units) of cracking heating surface

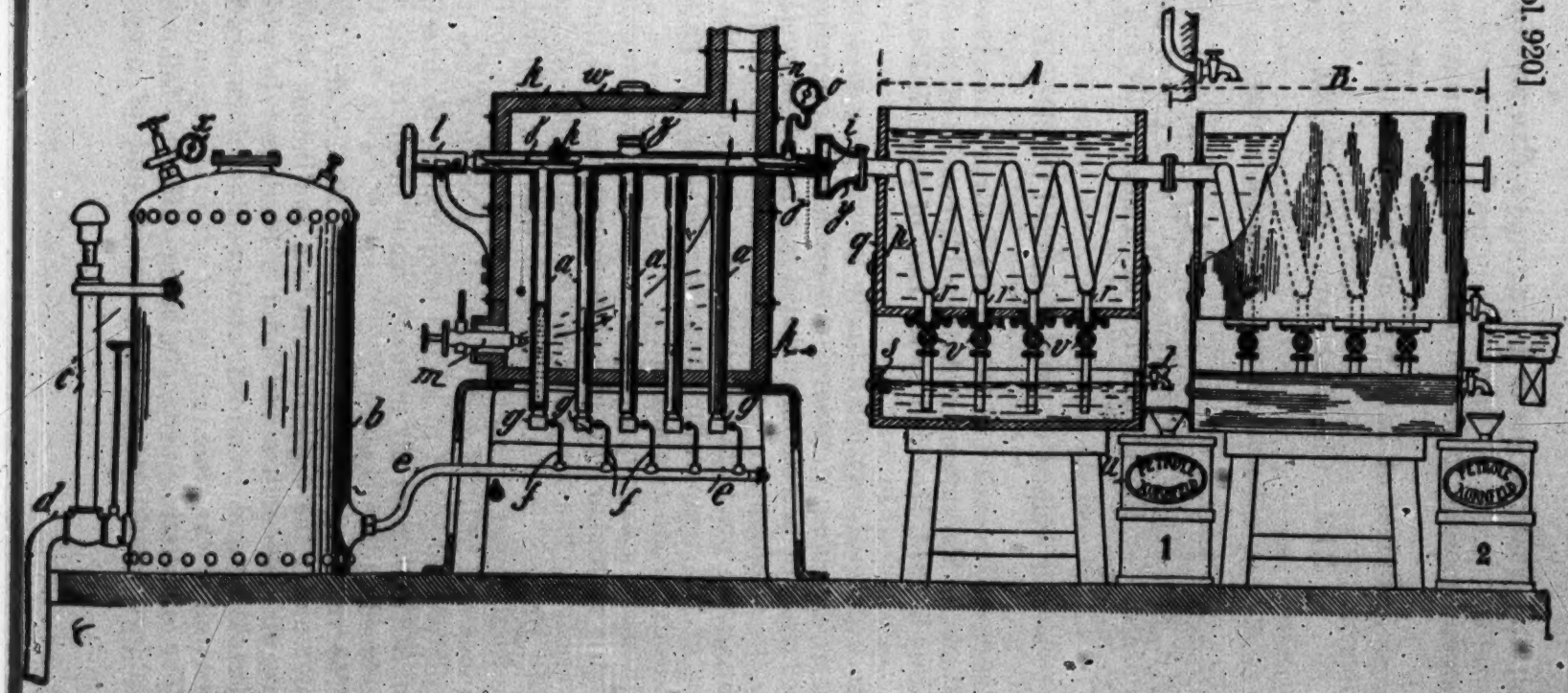
to the volume of oil not substantially less than 1:4.7, this ratio being derived when the inch is employed as the unit of measurement; substantially as described.

In testimony whereof we affix our signatures, in presence of two witnesses.

Raymond F. Bacon, Benjamin T. Brooks, Clinton W. Clark.

Witnesses: Geo. B. Nickel, S. C. Perring.

N° 338.051 M. Kerstein Pl. unique



[fol. 920]

4157

[fol. 921] TRANSLATION OF PETITIONER'S EXHIBIT No. 123

French Republic, National Office of Industrial Property

Patent of Invention of August 6, 1902

XIV.—Chemical Arts. No. 328,051

5.—Essences, resins, waxes, rubber

Patent for Ffteen Years Applied for August 6, 1902, by Mr. Kornfeld (Adrien-Ignace).—For Process and Apparatus for the Distillation of Mineral Oils and Other Materials.

(Patented August 6, 1903; published October 21, 1903)

(Patent of Invention of Which the Delivery Has Been Held Back in Execution of Article 11, Sec. 7 of the Law of July 5, 1844, Modified by the Law of April 7, 1902)

In a general way the actually known processes of refining or distilling of mineral oils consists in operating on a fixed mass of petroleum enclosed in a retort, in gently raising the temperature by heating towards 150° and in separating the products collected; then continuing the elevation of the temperature towards 250-280°, to gather up again the products obtained.

In short, a fixed quantity of mineral oil was successively carried to higher and higher temperatures and thus gave successively heavier and heavier distillation products.

My process is characterized in that the mineral oil is admitted, under pressure regulated at will, in a continuous manner and in little quantities into a boiler where it is immediately subjected to a high temperature to directly fur- [fol. 922] nish an all inclusive mass of all of the vapors produced under pressure.

The vapors generated under the said pressure leave the boiler under the same prssure in a continuous jet through a regulatable orifice and enter a condenser in which the withholding and fractional condensation of vapors is produced all of the time.

The distillation products being different following the combined conditions of temperature and of pressure to

which the mineral oil is subjected in my boiler, it is evident that by my process I am in a position to obtain distillation products with predominance, at my will, of such or such other of these products.

I have represented in the drawing, by way of example, an installation of the apparatus that I utilize for the carrying out of my process.

The boiler is composed of a series of vertical generator tubes of inclined tubes *a* in which the liquid petroleum is admitted at the base; the liquid petroleum comes under pressure from a feed reservoir *b* fed by means of the pump *c* which compresses into the reservoir *b* the petroleum coming through a conduit *d* from a cistern situated at any locality. The reservoir *b*, in which the air is compressed to the desired pressure above the level of the petroleum which is confines, is provided with manometer *x* indicating this pressure; this reservoir is connected by a distribution tube *e* to tubes *a* by means of little tubes *f* placed spaced on the conduit *e* and opening into the tubes *a* by means of a stopper connection *g* screwed to the base of these tubes.

All of the tubes *a* communicate at their upper ends with a collector *h* consisting preferably of a tube to the interior of which the vapors formed in the tubes *a* proceed and placed to permit the regulation of the pressure of these vapors; these vapors can escape from the collector *h* through an orifice *i* in which the point of a rod *j* penetrates, forming a regulating point and permitting the varying of the size of the section of the orifice *k* and even of completely closing this orifice. The regulating rod *j* is operated at the opposite end of the collectors *h* by a key 1 forming a movable screw on the threaded end of the collector; this key is provided with a wheel for hand operation.

The exit orifice *i* can be regulated by any other means capable of reducing this orifice with a view to maintaining in the boiler (tube *a* and collector *h*), the desired vapor [fol. 923] pressure and to avoid all relaxing of these vapors before their departure through the orifice *i*.

A manometer *o* placed on the collector *h* enables the pressure which prevails in this collector be known at all times.

The organization of the boiler, that is to say, the tubes *a* and the collector *h* are enclosed in a chamber or fire box *k* of refractory tiles covered by a metallic mantle, for ex-

ample. The heating of the tubes *a* is obtained by placing in the chamber *k* one or many burners, for petroleum for example, such as *m* or by using the heat of any kind of fire box capable of *of* carrying and maintaining the tubes *a* at a high temperature. A chimney *n* permits the exhaustion of the products of combustion from the fire box.

The vapors then leave the collector *h* under pressure and proceed into the condensing apparatus.

The condenser is formed of several elements consisting each of a worm developing horizontally in a vat enclosing the cooling liquid.

The first element (A) of the condenser comprises a worm *p* placed in continuation of the orifice *i* of the collector to which it is connected by the receiving head *y*; the worm *p* is enclosed in a vat *q* filled with water for example; the condensed liquid can be gathered at the base of each of the turns of the worm *p* by means of little tubes *r* branching on these turns and passing through the bottom of the vat *q* to permit the liquid of condensation to flow out into a vessel *s* situated below the vat *q*. The liquid of the vessel, *s*, itself, forms a hydraulic closure for the tubes *r*, and this liquid maintained at a constant level is withdrawn through a valve to be placed in casks, for example, in bonbonnes *u*.

Each of the tubes *r* is provided with a valve *v* to permit of receiving in the vessel *s* liquid coming from one or the other of the turns of the worm *p* or simultaneously from several turns.

The vapors not condensed in the first element (A) of the condenser pass into a second element (B) similar to the first, the cooling water of the vats *q* of the various elements of the condenser is maintained at the temperature favorable to the condensation of products to be gathered in each element.

The products condensed in this second element (B) are necessarily lighter than those retained in the first (A), they are also placed in casks. One can thus place in succession enough elements of condensation as are necessary [fol. 924] to gather successively the lighter and lighter products contained in the mass of vapors admitted to the condensation.

It can happen that the mass of vapors admitted to condensation encloses a certain quantity of gas which does

not condense in the apparatus; I reserve to myself to utilizer this gas for the heating of the boiler concurrently with the too light liquids, such as gasoline.

I can hasten the condensation of the vapors by piercing some openings in the receiving head *y* by which the vapors leaving under pressure from the orifice *i* entrain exterior air which suddenly lowers the temperature of the said vapors.

The residues contained in the petroleum and which has not been volatized remain in the tubes *a*; from time to time it is necessary to remove these residues. In the case where the decomposition of the petroleum has been pushed up to the formation of coke, this deposits on the walls of the tubes *a*. The cleaning of these tubes is effected by means of a borer or scraper calibrated to enter these tubes; an opening with a stopper *z* can be arranged on the collector and opposite each tube to permit the cleaning tool to be introduced through this opening.

I can, besides, arrange my boiler in any convenient manner, and particularly I can have on a single collector as many generator tubes as are desired; I can also arrange my boiler in such a way that the tubes *a* are alone enclosed in the heating chamber while the collector will be placed outside this chamber.

Claim

The process for the distillation of mineral oils and other materials and the apparatus permitting the realizing of the process that has been described above, in substance and represented by way of a specimen in the annexed drawing.

P. Caquet, by M. Kornbield, Attorney.

Fig. 1

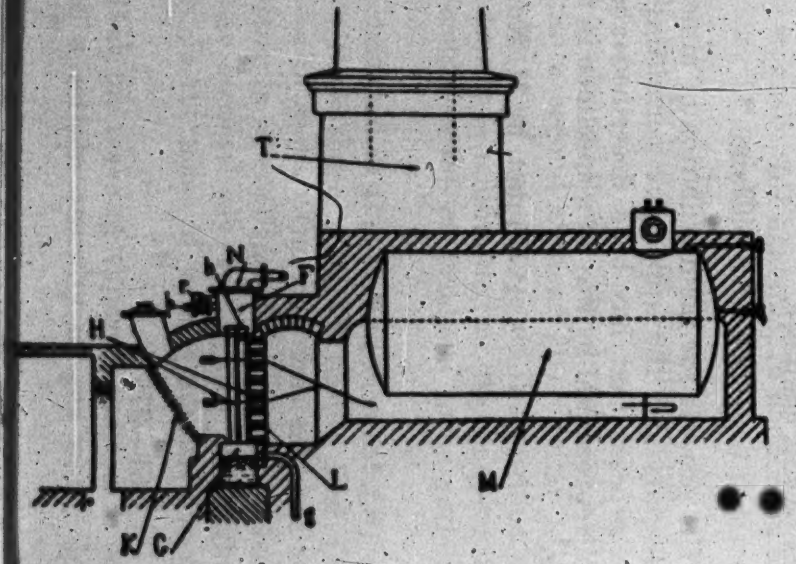


Fig. 2

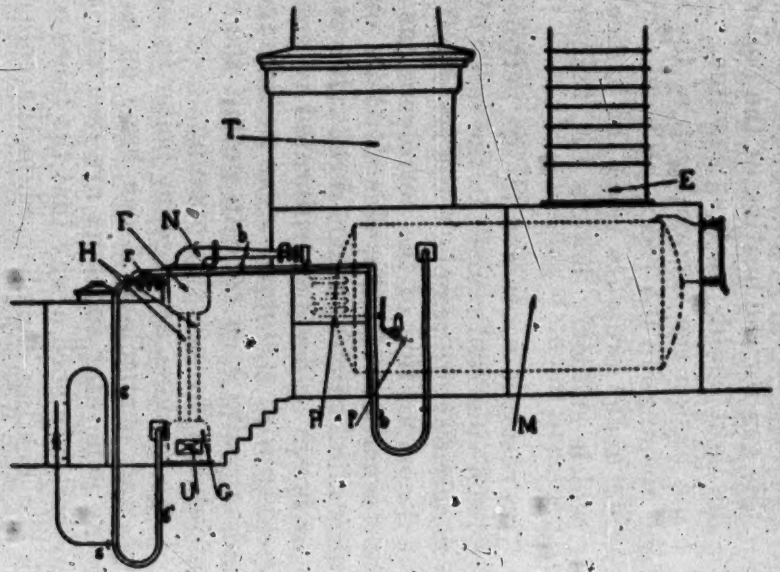


Fig. 1

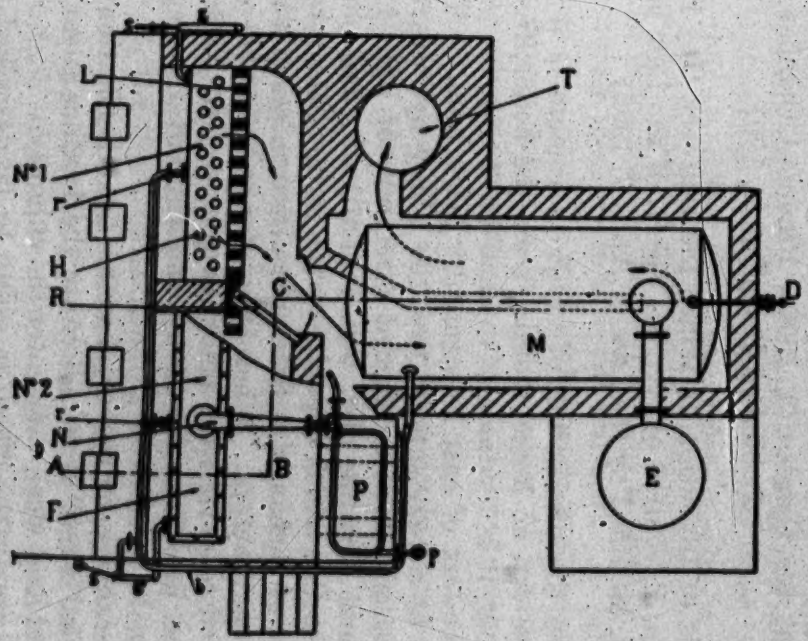


Fig. 4

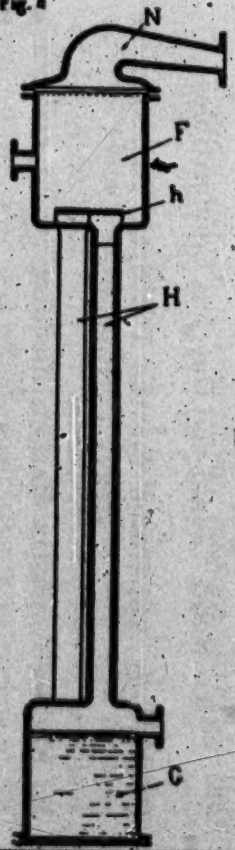
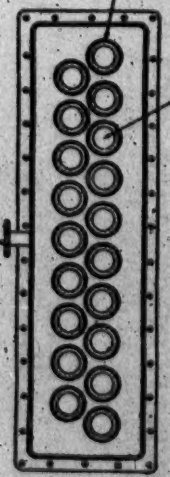


Fig. 5



[fol. 926]

4163

[fol. 927] Translation of Petitioner's Exhibit No. 124

French Republic, National Office of Industrial Property

Patent of Invention

XV.—Lighting, Heating, Refrigeration, Ventilation. No. 380,282

3.—Solid, Liquid and Gaseous Combustibles

Continuous Apparatus for the Pyrolytic Dissociation of Heavy Petroleums

M. Emile—Augustin Barbet, Residing in France (Seine).

Applied for October 3, 1906. Patented October 4, 1907. Published December 4, 1907

(Patent of Invention of Which the Delivery Has Been Put Off in Execution of Art. 11, Sec. 7, of the Law of July 5, 1844, Modified by the Law of April 7, 1902)

When the distillation of crude petroleum is terminated and one can no longer obtain, from the boiler, lighting oil products, it is customary to send the residuum into other large boilers of cast iron called "Black pots." There, by means of a very intense fire, the heavy hydrocarbons are dissociated; there is formed a mixture of light hydrocarbons and lighting oils, which distill off, and some very dense carbon which deposits on the walls of the retort. The deposit of carbon is at times permitted to reach a thickness of 50 centimeters. When it is stopped, several days are required to permit the retort to cool so that workmen can descend into it to break up and lift out the deposits of carbon.

One can say, moreover, that this final distillation requires an actual waste of coal because the heating gases are still at a red heat when they enter the chimney.

The apparatus which is going to be described proceeds on an entirely different principle. It is continuous, and as such it can with advantage complete the continuous rectifier of petroleum described in French patent No. 322,265 of June 7, 1902.

Figures 1, 2 and 3 represent in section, in elevation and [fol. 928] in plan the new dissociating apparatus combined with a continuous rectifier E which is provided with a cylindrical boiler M.

At one of the ends of the boiler are installed two like dissociators designed to operated alternatively. From the boiler the liquid to be dissociated passes to one or the other of the dissociators in a continuous manner through the siphon-tube *b* and the valves *r* or *r'*.

Each dissociator, figures 4 and 5, is composed of two reservoirs of plate iron or better of cast iron F and G, connected by a certain number of vertical tubes H of sheet steel, in which the heavy oil to be dissociated descends by running down. For this effect, each tube is provided at its upper part with an adjustable ajutage j which is notched; all of the ajutages are regulated for the same level, in such a manner that all of the dissociator tubes receive in a unit of time the same quantity of oil to be dissociated.

All of the tubes receive the direct effect of the fire box K which can bring them to an incipent red heat. At the rear of the tubes H is placed a wall with openings of refractory bricks L, figures 1 and 3, for the purpose of heating the rear of the tubes as well as the front and the lower part as well as the upper.

The upper reservoir F is closed by a cover forming the dome N of the alembic, which is con-ected to a cooling worm P, closed by a gauge glass *p*.

The lower reservoir G possess an exit tabulature *g'* with a downwardly extending siphon tube the rising branch *g* being placed to obtain an emulsion.

Things being thus arranged, if one feeds the reservoid F regularly and continuously with the oily residues leaving the boiler M, the liquid goes running downward along the superheated walls of the tubes, and the dissociation proceeds to take place forming a deposit of carbon, of which a part will attach itself to the tubes and a part will descend into the reservoir G especially if the feeding of oil is greater than the dissociating power of the tubes.

This excess feed is not difficult to realize; let us suppose that for some moments, due to a start in advance taken by the rectifying boiler M, one feeds F at a rate of three or four times the quantity that can be dissociated. It will

result that one volume will be dissociated and two others will descend undissociated into the lower reservoir G. But there is an emulsifying siphon *gg'* with the injection of steam at *s;* at the temperatures there, the steam acts as an [fol. 929] incondensible gas. It makes the excess oil rise up into the reservoir F to recommence the dissociation whereas, the steam, assisting in the disengatement of the volatile products of dissociation through N, will condense with them in the worm P.

When the tubes of dissociator No. 1 are obstructed with carbon, the second dissociator is placed in operation and the first is stopped. For that the pivoted register R will be turned into the second position. The gas from the second fire box flows through under the boiler M exactly in the same course as before, there will be no change at all in the pace of the continuous rectifier. The hot gases go to the chimney T.

The cover of the first dissociator is opened to clean it; the notched adjutages *h* are drawn out and trepan is passed into each tube H to detach the carbon. This falls into G and from there is drawn through the man hole U. This cleaning is by no means laborious, the men not having to enter the apparatus. Moreover it is very rapid.

The dissociating power of the tubes can be still further increased by causing several long iron chains to hang in each tube, along which the liquid will flow downwards at the same time as on the walls themselves of the tube.

The products of dissociation, leaving through the gauge glass *p* are ordinarily turned into the crude oil to return to the continuous rectifier. One can still send the vapors directly into the rectifier, but the dissociator apparatus will be less easy to operate because one can not take account of the working of the furnace by itself neither as to quantity nor as to quality.

Claims

The process of dissociation realizes continuity of operation throughout long periods. The arrangement permits, if one so wishes, of making the two dissociators operate simultaneously by placing the register in the axis of symmetry.

The dissociation by flowing down on strongly heated walls is very radical and very rapid; the transmission of

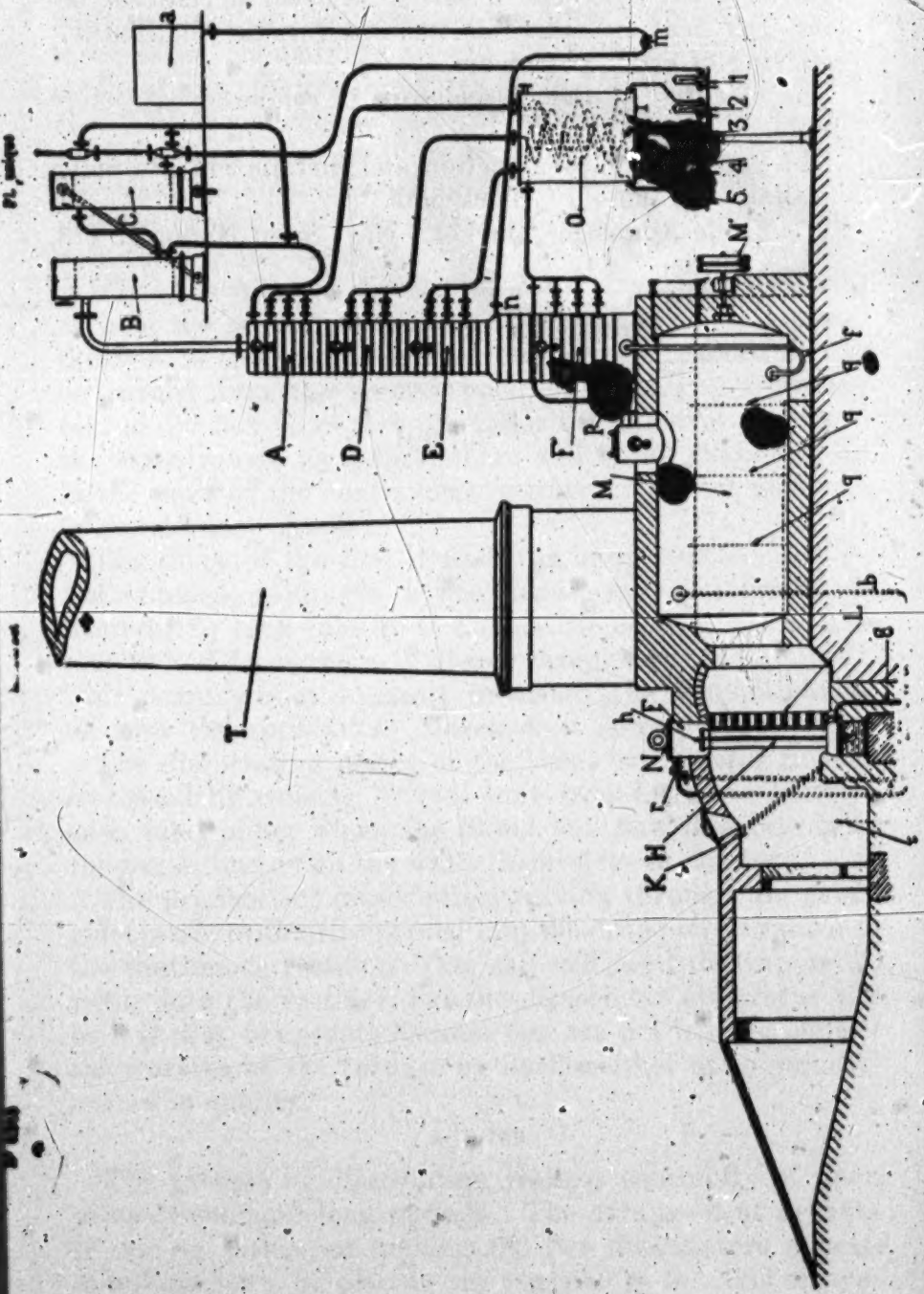
the heat of the heating is much better because the accumulation of great thickness of carbon is never permitted; besides, the heat in excess is utilized for the distillation-rectifying of crude petroleum.

The cleaning of the dissociators is rendered extremely simple.

The expenses of construction and installation are much less than with the old "Black pots."

Emile-Augustin Barbet, rue Saint-Honoré, 173, Paris.

[fol. 930]



[fol. 931] TRANSLATION OF PETITIONER'S EXHIBIT No. 125

Translation of addition 8213 to French Patent 322,265 to Emile-Augustin Barbet, applied for December 1, 1906, granted Dec. 3, 1907, published February 8, 1908.

Process and apparatus for continuous rectification of petroleum and volatile hydrocarbons.

Patent No. 322,265 applied for June 7, 1902 described a continuous rectifying apparatus for petroleum with three parts: extraction of volatile liquids, extraction of lamp petroleum and decomposition of heavy oils.

This apparatus can be simplified according to the accompanying drawing which will be explained at present. The crude petroleum is pumped into tank *a*. From there it is regulated by the feed cock *m* and at *n* it enters the plate column. It descends through the plates F′ which are hot enough for boiling and there it is freed first of all its volatile liquids which rise into the upper plates.

The light vapors rise to condenser B which causes them to return to the top of the column. The most volatile parts, uncondensed, pass into cooler C and then to gage 1. The returning liquid is subjected to true separation in the plates of the column. In the upper parts A, a very light liquid of density less than 0.700 can be extracted. A little lower at D, a little more dense quality is found and the last gasolines boiling at 12-130 deg. are extracted at E.

The extracted liquids are boiling; they are cooled in cooler O and leave respectively through gauges 2-3 and 4.

All these extractions take place in liquid form, in agreement with the principle stated in the patent; the plates have only a liquid condensed after distillation, that is to say, clear and limpid, which can be sold directly.

In the lower plates F′ on the contrary, crude petroleum circulates; thus the extractions can no longer be made in the liquid form because the liquid would be dirty; but once this liquid has boiled on a certain number of plates, and that it is thoroughly freed in this way from all its light products, lamp oil products thoroughly freed from volatile oils are obtained if vapors are taken from one of the lower plates F′.

[fol. 932] At the bottom of F, crude petroleum descends through pipe *f* ino boiler M which acts as source of heat.

This boiler is heated by flames whose origin will be described below. All the lamp oil products are distilled and passed into Column F but the temperature of the boiler is not sufficient to cause dissociation of the heavy oils.

If desired, lamp pertoleum vapors can be extracted directly from the boiler M. that is, to say through cock *p*. The boiler can be furnished with an agitating mechanism M' for facilitating the liberation of the petroleum vapors.

Is is well to furnish the boiler with inner diaphragms *q* arranged in such a way that the heavy petroleum passes regularly from the front of the boiler to the rear being freed more and more from its lamp oil.

The outlet of the worked crude petroleum takes finally through pipe *b*. If it is desired to extract and purify veselines and paraffines, the heavy oil is led as it is to the extraction plant for these products.

But if it is desired to carry on "cracking" or thermal dissociation of the heavy oils, there will be added to the apparatus the tubular continuous dis-ociation apparatus described in the patent filed October 3, 1906. This special dissociating apparatus is sketched with the same reference letters as in the above-mentioned patent.

Fire will thus be made on the slanting grate K and the flames will energetically attack the cast tubes H in which flows the heavy oil to be decomposed or dissociated.

The flames pass from there under boiler M and circulate two or three times before going to chimney T.

The products of decomposition coming from dissociating apparatus H cannot enter boiler M for several reasons:

1. Information could not easily be had of the correct operation of the dissociating apparatus:

2. The superheated steam injected into the dissociation apparatus for aiding in the cracking, after having passed through the boiler M would go into the plate column F' E D A and there cause dangerous disturbances for it must not be forgotten that the bottom of F' is at about 300 deg; while plates A are much lower than 100 deg.

3. Cracking produces lamp oil and volatile oils at the same time; thus the vapors liberated from M would *on* longer be composed exclusively of lamp oil.

For all these reasons, the dissociating vapors should be sent into a separate coil as described in the patent. But the [fol. 933] condensed products will be sent back into the crude petroleum to be admitted with it into the column at *n* where the separation of the volatile liquids and the lamp oil will take place as with the crude petroleum itself.

Summary

The object of the present invention is:

1. To describe a simpler continuous column than the combination of the main patent in regard to fractionating the various classes of gasoline and lamp oils;

2. To substitute for the primitive methods of treating heavy oils described in the patent, the thermal method of dissociation more recently patented;

3. To show finally how this final treatment of continuous thermal dissociation can and should be combined and connected with the continuous rectification apparatus for volatile liquids and lamp oil, but without the products of dissociation going back directly to the large distillation boiler.

Tr. MMJ.
8-21-25.

[fol. 934] PETITIONER'S EXHIBIT 126

W. G. Warden,
Oil Still

No. 110,806. Patented Jan. 3. 1871

Fig. 1.

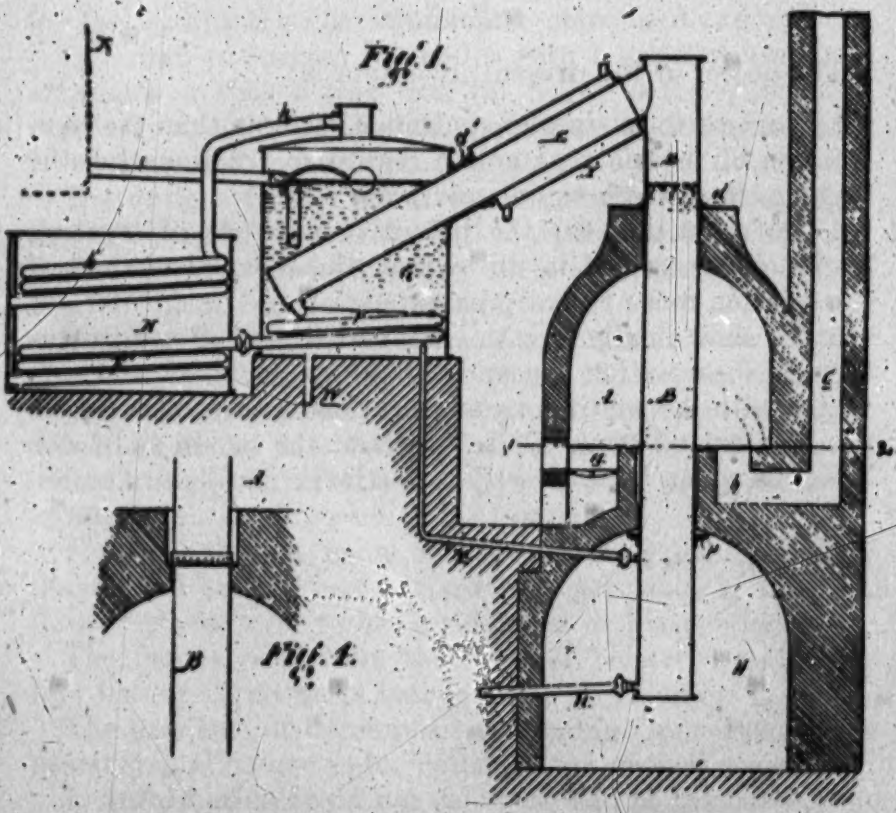


Fig. 4.

Fig. 3.

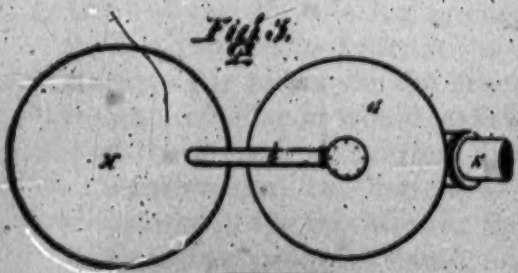


Fig. 2.

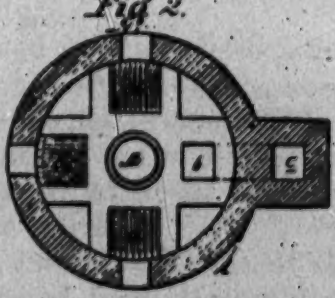


Fig. 5.

WITNESSES: Henry Smyth
Robert Parker

W. G. Warden
by his Attorneys and Solicitors

PX 126-1

[fol. 935] United States Patent Office

William G. Warden, of Philadelphia, Pennsylvania

Letters Patent No. 110,806, dated January 3, 1871

Improvement in Apparatus and Processes for Distilling Oil

The Schedule Referred to in These Letters Patent and Making Part of the Same

I, William G. Warden, of Philadelphia, county of Philadelphia, State of Pennsylvania, have invented an Improved Oil-Still, of which the following is a specification.

Nature and Object of the Invention

My invention consists of an oil-still constructed and operating in a manner too fully explained hereafter to need preliminary explanation, the main object of my invention being the extraction of all the volatile matters from the oil, the saving of fuel, the preservation of the still from rapid destruction by the action of the fire, and a continuous distillation when desired.

Description of the Accompanying Drawing

Figure 1 is a vertical section of my improved oil-still;
Figure 2, a sectional plan of the furnace on the line 1 2;
Figure 3, a plan view of condensers;
Figure 4, a vertical section, illustrating a modification of my invention; and
Figure 5, a diagram illustrating another modification.

General Description

A is the furnace, which, in the present instance, is of a circular form, and at the base of which are three fire-places, *a a a*, all communicating with the interior of the furnace and with a flue, *b*, by which the products of combustion are carried off to the chimney, *c*.

On the arched top of the furnace bears a flange, *d*, secured to the still B, which consists of a long hollow cylinder of plate-iron or steel, the said cylinder passing entirely through the furnace, through the base of the same, and terminating within a chamber, D, formed beneath the furnace.

A pipe, 1, extends from the upper end of the still B, through a stuffing-box, *d'*, on the tank G, and, within the latter, communicates with a worm, F, the tube of which passes into another tank, H, containing cold water, and is there coiled into another worm, F', and finally passes through the said tank.

From the top of the tank G a pipe, *h*, passes into the tank H, is there coiled, and passes from the tank, as shown in fig. 1.

Oil is introduced from an elevated reservoir, X, into the tank G, through a pipe, *i*, bent at the end, and furnished with a cock connected to a float-lever, by means of which the oil is maintained at a uniform heat in the tank, the same level being maintained in the still as the process of distillation continues, owing to the pipe *m*, which affords a direct communication between the said still and the lower portion of the tank G.

Ordinary petroleum-stills consist of large vessels, directly to the under side of which the products of combustion are applied and from the bottom of which the residuum is withdrawn through what is known as a "tar-pipe," which extends below, and is protected from the fire. Owing to the application of the heat to the lowest part of the still, an incrustation of the residuum collects on and adheres to the bottom of the vessel to such an extent that not only is an enormous quantity of fuel required to impart the desired heat to the still, but the rapid destruction of the latter, owing to the presence of the nonconducting incrustation, takes place.

It will be observed that a portion only of the still B is exposed to heat in the fire-chamber of the furnace, the lower portion below the same being a receptacle for the retention of the residuum, which, being free from exposure to direct heat, cannot become incrusted, but may be drawn off, in a fluid or semi-fluid state, through the pipe *n* when the still is to be cleansed.

A flange, *p*, is secured to the still, at or near the roof of the chamber D, and the hole in the base of the furnace, through which the still passes, is larger in diameter than the still itself, so that there may be an intervening annular space for the reception of a body of sand, which, resting on the flange *p*, will form a sufficiently tight joint to prevent air from gaining access to the furnace from the chamber

below. At the same time the packing will permit the still to expand and contract without injuring the base or other part of the structure of which the furnace is composed.

If desired, a packing of clay might be interposed between the flange *p* and the roof of the chamber D.

As the oil of the tank G is exposed to the heat of the vapor-pipe E and worm F, it will be deprived of its water and other impurities, which may settle at the bottom, and can be drawn off through a cock, *w*. At the same time the heat of the oil in the tank G is not too great to prevent it from acting as a condensing or partially-condensing medium for the vapor which passes through the worm F, the complete condensation being accomplished in the worm F′, which is exposed to the cold water contained in the tank H.

The heat imparted to crude petroleum in the tank G will be sufficient to give off benzine vapor, which, passing through the pipe *h*, will be condensed in the worm *h′*, contained in the water-tank H. This worm and pipe will not be needed in distilling tar or residuum of crude petroleum, although they could be used to advantage when the residuum has been mixed with heavy benzine for re-distillation.

Different qualties of oil require different degrees of heat to enable it to throw off the benzine in the tank G. When a greater heat is required for this purpose than that afforded by the vapor-pipe, I introduce steam or superheated steam [fol. 936] into a coil in the tank, to facilitate the generation of benzine vapor; and when the heat of the vapor-pipe E is too great, I introduce into a casing, V, which surrounds it, cold water, the water entering through a pipe from below, and escaping through another pipe above, and the circulation of the water being regulated in accordance with the desired temperature of the oil in the tank G.

One of the most important features of my invention is the peculiar arrangement of the still within the heating-chamber of a furnace—an arrangement which tends to preserve the still, and lessens the consumption of fuel, while that portion of the still beneath the point where the fire is applied affords a receptacle below the fire of such a size as to retain all the heavier particles from which the volatile matters have been removed. This arrangement may be modified, as shown in fig. 4, in which case the still is sup-

ported on the base of the furnace; or the still may rest with its extreme lower end on an appropriate foundation, in both of which modifications it will be necessary to so joint the vapor-pipe E as to permit the upward expansion of the still when exposed to heat. For this reason I prefer to support the still on the roof of the furnace, so that it may be at liberty to expand downward without disturbing the vapor-pipe.

In some instances the still may be inclined instead of vertical, as illustrated in the diaphragm, fig. 5, the arrangement of which will be readily understood without explanation; in all cases, however, the important feature of exposing the central portion of the still only to the fire, so that the portion below may be a receptacle for retaining the residuum, being in all cases adhered to.

It will be seen, without further description, that the process of distillation is continuous in the apparatus above described.

In ordinary stills the oil is generally introduced at or near the top, so that the heavier matters, which gradually settle to the bottom, are not disturbed, and, being subjected to a constant excessive heat, become coked, coating the heated portions of the still to such a thickness as to effectually prevent the transmission of heat to the remaining contents of the still. On cleansing the still these heavy matters are withdrawn, and are subsequently subjected to a second process of distillation to remove the volatile portions; these operations being repeated until all, or nearly all, the volatile matter is extracted. By my improvement this result is effected at one operation, for the continued introduction of the oil at or near the bottom of the still, through the pipe *m*, causes a current, which carries upward the heavier matters, so that the entire body of fluid within the still is caused to traverse the heated sides until every part which can be volatilized is removed; such heavier particles as no further heating will affect remaining in the chamber below the fire until the still is cleansed.

It will be apparent that this current to carry upward the heavier particles from the receptacle may be created by other means.

Another important feature of my invention is the application of heat to the vertical parts of the still, which thus afford no lodgment for the heavier matters, so that in-

crustation is prevented and the efficiency of the entire heated surface of the still is maintained.

Claims

1. The process of distilling oils, &c., by subjecting the same to the action of heat in a vessel, a portion of which extends below the fire, and in which a constant upward current from the said lower portion is maintained, as described.

2. An oil-still suspended or otherwise arranged within a furnace, so that a portion of the body of the still will project below the fire-chamber, forming a receptacle for retaining the heavier particles below the point where the heat is applied.

3. The combination of the subject-matter of the preceding claim and a feed-pipe *m*, communicating with the still near the bottom of the same, as set forth.

4. The combination of the furnace A and its fireplaces, the chamber D, and still B, supported on the roof of the furnace, and passing through the same into the said chamber D.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

William G. Warden.

Witnesses: Harry Warden, Wm. A. Steel.

[fol. 937] PETITIONER'S EXHIBIT 127

British Patent No. 6739, A. D. 1901

Complete Specification

Improvements in and Connected with the Distillation or Utilization of Tar, Pitch, Petroleum and other Hydrocarbon Mixtures, and the Extraction of Carbon Suitable for the Manufacture of Electrodes, Calcium Carbide, and other Industrial Products

I, Leon Gaster, Electrical Engineer, of 37, Maida Vale, in the County of London, do hereby declare the nature of

this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:

It is known, that tar usually contains more or less free carbon in suspension, which carbon retards the distillation, and at the higher temperatures, when the specific gravity of the liquid has been reduced by expansion, the carbon forms a deposit; it is desirable therefore, to separate the free carbon from the tar, whereby at the same time the wear and tear of the apparatus is reduced, and the quality of the bye products is improved.

Attempts have been made, to separate the free carbon from coal gas tar before distillation, by first mixing the tar with light oils, and causing the mixture to enter a highly heated retort, in order to deposit the carbon on the walls of the retort. It was proposed to scrape off and collect the carbon thus separated, in order to use it for electrical purposes. The oils which would be evaporated in such a retort, and could be subsequently recovered by means of condensers, consists partly of the light naphtha or other volatile oil which had been used as a solvent, and partly of the other constituents of tar, such as heavy naphtha, anthracene and other heavy oils.

If the retort contains a mixture of tar and volatile solvent, the cooling or pitch collecting pot into which the vapours pass from the retort, will contain not only the condensed heavy or pitch oils, but also the intermediate oils, that is to say, the major portion of the oils, which are heavier than the solvent used, but lighter than the heaviest pitch oils, boiling above 270° C. In order to separate these intermediate oils from the pitch oils, the mixture must be subjected to distillation in a separate distilling apparatus, [fol. 938] and as the separation only takes place at a high temperature, a portion of the oils contained in the mixture will be decomposed, thereby again forming free carbon which contaminates the mixture and has to be separated.

In order to avoid these defects, I extract the carbon at an intermediate stage in the distillation of tar, derived from ordinary gas works or coke ovens, or from any other source, that is to say, I first distil the tar until it approaches or attains the consistency of pitch, which usually occurs at a

temperature above 260° C., I then interrupt the distillation and add to the partly cooled pitch left in the still a sufficient quantity of naphtha or other light oils for dissolving the major portion of the viscous matter contained in the pitch. The quantity of volatile solvent to be mixed with the pitch depends on the quantity of pitch and the nature of the solvent, and is therefore variable within wide limits. As a rule, 1 kilo of pitch for 1 to 3 litres of naphtha is a suitable proportion. When the solvent is added to the hot pitch and allowed to act, some of the solvent may be caused to evaporate by the temperature of the pitch, and the vapours thus formed are condensed for subsequent use; I separate the free carbon from the mixture of solvent and pitch by means of a heated retort, which receives the mixture either directly from the mixing vesesl, or after a partial sparation of the free carbon has been effected by allowing the mixture to stand, or by treatment with a centrifugal machine or other mechanical means, as will be hereafter described with the aid of the drawings.

In the retort the volatile solvent and the heavy oils (pitch) are separated in the shape of vapours from the free carbon, and are conducted to a cooling or pitch-collecting pot, where the heavy oils (pitch) are collected, and, if necessary, are mixed with other oils like creosote, anthracene, etc., for obtaining the desired quality of the pitch, that is to say soft or hard pitch, or pitch having the desired softening point, adhesiveness and consistency, according to its particular application, such as the manufacture of block fuel or varnish, etc.

If, however, the retort contains a mixture of tar and solvent, instead of pitch and solvent, the cooling or pitch-collecting pot will contain a sufficient quantity of intermediate oils to render a subsequent distillation necessary.

Moreover, if a mixture of tar and solvent is supplied to the retort, the solvent has to dilute not only the pitch oils, but also the intermediate oils, consequently more solvent, (about 30% more) will be required for diluting the tar [fol. 939] necessary for obtaining a given quantity of free carbon than for diluting the pitch necessary for obtaining the same quantity of carbon, and the capacity of the retort, stills and auxiliary apparatus must also be greater.

If pitch is used instead of tar as a raw material, the subsequent separation of the volatile solvent from the mixture takes place easily and completely, without decomposition of hydrocarbons and consequently without formation of free carbon, and the pitch resulting from the separation is therefore superior to ordinary pitch as regards its applicability to the manufacture of black varnish, or as a binding substance in the manufacture of block fuel.

In the accompanying drawings:

Fig. 1 is a vertical section of a mixing vessel, intermediate receptacle, retort and auxiliary appliances embodying my invention.

Fig. 2 is a plan of the same.

Figs. 3, 4 and 5 show on a larger scale the apparatus for regulating the supply of liquid to the retort.

Fig. 6 is a section of a water-cooled nozzle for supplying the liquid to the retort.

Fig. 7 is a vertical section of a safety device, through which the vapours may escape safely, if their pressure exceeds a certain limit.

Fig. 8 is a horizontal section of a retort showing the construction of the scraper.

Fig. 9 shows the construction of a float with three-stage alarm apparatus for the intermediate tank, serving to supply liquid mixture to the retort.

Fig. 10 shows an optical alarm apparatus which may be used in combination with a float indicating the level of the mixture in the tank.

Fig. 11 is a side view of the condensing apparatus for the vapours and gases which come from the heated retort and which pass through the pitch-collecting pot.

Fig. 12 is a plan of the same.

Fig. 13 is a plan of apparatus necessary for extracting the carbon from the pitch or tar and oil mixture by means of a filter press process, instead of a heated retort.

Fig. 14 is a side view of a filter-press plant, showing the various connecting pipes and necessary apparatus.

Fig. 15 is a partial longitudinal section of a filter press on a larger scale showing the various connecting pipes.

Fig. 16 is a cross section of the filter press casing and end view of the filter press.

[fol. 940] Fig. 17 is an end view of the filter press and casing.

The retort employed is preferably upright and cylindrical, such as the retort 1 in Fig. 1, to which the mixture of pitch and volatile solvent is supplied through pipe 2, care being taken, to avoid the admission of air. The retort is provided with a stirrer chiefly consisting of a vertical shaft 3 provided with radial arms 4, carrying the blades or scrapers 5 through the intermediary of a hinge piece 6 (Fig. 8).

I obtain the desired distribution of the mixture by forcing it at a suitable pressure downward or upward through a nozzle, or through several nozzles distributed along the walls. In Fig. 1 the supply pipe 2 has 3 branches 7 leading to three nozzles. And as the high temperature in the retort might cause carbon to separate in the nozzle, so as to choke the same, I provide each nozzle 8 with a cooling jacket 9, Fig. 6, through which cold water or other cooling agent is caused to pass by means of a suitable feed or circulating pipe 10. The interior of the nozzle may also be provided with a guide screw 11. Before the mixture reaches the nozzle, it should pass through a sieve, in order to hold back any solid particles, which might be liable to choke the nozzle or the regulating valve or cock.

In the drawings Figs. 1 and 2, the supply pipe 2 has its inlet a short distance above the bottom of the intermediate tank 28, and extends above the said tank, where it forms three parallel branches 13, provided with stop-cocks, and two of them with strainers 12. Only one of the three branches would be used at a time. 14 is a double-acting pump inserted into the pipe 2, to feed the retort with the mixture.

As the heating capacity of the retort for the extraction of the free carbon depends partly on the motion of the scraper for keeping the sides of the retort clean, the supply of the mixture to the retort should be regulated automatically, which may be effected by a regulating tap 15 (Figs. 3 and 4) controlled by a centrifugal governor 16 or other means adapted to stop the supply of the mixture, when the scraper stops, and thereby to avoid the clogging of the powdered free carbon, and as the mixture remaining in the supply pipe after the tap has been turned off might thicken

and tend to clog the pipe, I provide a supply of ordinary or superheated steam or oil under pressure, which may be controlled by the governor or other means, so as to clear the pipe of the mixture, after the tap has been turned off, making it ready for a new start without further delay. [fol. 941] In the drawings the movable disc or ring 17 controlled by the governor balls, carries a pair of vertical guide rods 18, adapted to act on the lever 19 controlling the tap 15 and on the lever 20 controlling the tap 21. The former is inserted into the steam pipe 22, and adapted to supply oil or steam to the pipe 2 and nozzles, as soon as the tap 21 has been turned off.

The scraper must be capable of easy adjustment, so as to compensate for expansion and contraction, caused by differences of temperature, and also for the wear and tear of the blades.

For this purpose the blades 5 of the scraper Fig. 8 are placed at an acute angle to the walls of the retort 1 and fixed to arms 6 which are hinged to crossheads 4 mounted on the scraper shaft 3, so that the centrifugal force of the revolving scraper tends to keep the blades in contact with the retort.

Each of the hinge joints is provided with an abutment, which allows the hinged arm 6 to turn only through a small angle, so that the line connecting the edge of the scraper blade 5 with the axle of the hinge must always form an angle with the radius of the retort passing through the said edge. The screws which secure the scraper blades 5 to the arms 6, pass through slots, or other means may be adopted to render the position of the blades adjustable according to the wear and tear of the blades.

Without automatic adjustment of the scrapers the walls of the retort are liable to become increasingly coated with carbon, whereby the transmission of heat to the contents of the retort would be impeded and the working of the apparatus rendered inefficient.

The carbon scraped off the walls of the retort 1 drops into an intermediate chamber 23 provided with a sliding door at the top and one at the bottom, (not shown) which doors may be mechanically connected in such a manner, that one of them must always be closed before the other can be opened, so as to prevent the access of air to the retort. In-

stead of two sliding doors, other suitable devices may be adopted for excluding air, and from the intermediate chamber the carbon is allowed to drop into a truck 24 placed underneath the same. If the retort extends above the nozzles 7, that part which is situated above the nozzles may contain straining plates or other suitable straining devices, through which the vapours generated in the retort ascend into the vapour and gas outlet, while any particles of carbon which may have been carried up by the steam are held [fol. 942] back and caused to drop again to the bottom of the retort.

A separate pipe for oil or steam under pressure may be provided also for clearing the strainer, or other parts of the apparatus liable to get stopped or clogged.

Instead of forcing the mixture through a nozzle or nozzles at a high pressure, it may be injected into the retort from above by means of ordinary or super-heated steam passing through an injector.

The vapours generated in the retort 1 are led off at the top through 2 branch pipes 25 into a tube 26 or a condenser leading into a suitable separating pot or pitch collector 27, (Fig. 1), the heavy oils or pitch devoid of free carbon being allowed to settle at the bottom and run off, after having reached a certain level, and care being taken to prevent the access of air, while the light vapours are led off at the top to one or more condensers, and uncondensable gasses are burnt or otherwise utilised.

To prevent air from entering the retort through the feed pipe and nozzle, the mixture of pitch, solvent, and free carbon may be supplied to the retort from an intermediate reservoir 28, Fig. 1, which is provided with a float 29. This float may operate an alarm apparatus and a valve 30 (Fig. 9), intercepting the communication between the reservoir 28 and the retort 1, when the level of the liquid mixture drops to an allowable limit.

Fig. 9 shows an acoustic three-stage alarb, consisting of a vertical rod 31 provided with three arms 32, 33, 34, adapted to strike a lever 35 and thereby to operate the striker 36 or a gong 37. It also shows a modification of the means for supplying the liquid to the reservoir 28 and for delivering the liquid.

In the normal position of the float 29, the three arms are situated some distance above the lever 35; if the float drops, the lever 35 will first be depressed by the arm 34, then by the arm 33, and finally by the arm 32, and every time the gong 37 will be struck by the level 36. In the drawing 28^a is the liquid outlet from the retort to the reservoir, 28^b is the supply pipe for compressed air, which forces the liquid out of the reservoir, so that no pump need be used. 28^c are steam or air jets for stirring up the liquid in the reservoir 28. The liquid is supplied to the reservoir 28 through the bottom by means of pipe 28^a.

The optical alarm apparatus or liquid level indicator represented by Fig. 10 chiefly consists of a float spindle 31^a [fol. 943] which extends into a graduated glass tube 35^a and carries at the top a coloured disc 21^b, easily visible through the glass. The glass tube 35^a is closed at the top and held by a metallic arm 35^b fixed to the liquid reservoir containing the float.

Figs. 1 and 2 show an alternative safety device controlled by the float 29. It consists of a bellcrank-lever 28^1, one arm of which rests against the spindle 29 of the float 29^1, while another arm is connected by a chain 28^{11} with the disengaging gear of the pump, and also with a steam valve connected with the feed pipe leading to the nozzle in the retort. The said bellcrank lever is connected with a weight 31 or a spring which tends to pull the said chain, as soon as the spindle of the float allows the bellcrank lever to turn. This occurs, when the float has descended to the allowable limit, drawing the float spindle 29^1 out of contact with the lever, whereupon the supply will be stopped and steam admitted to the feed pipe and nozzle, so as to clear the same and make them ready for another operation. At the same time the said chain may operate an acoustic alarm, not shown in the drawing.

The said pump disengaging gear, steam valve and alarm may be of known design, and are therefore not shown in the drawings.

The oil mixture may be supplied to the nozzle from an intermediate reservoir which is placed at a higher level or subjected to air pressure, or it may be forced through the nozzle by means of a pump 14, as shown in Fig. 1.

The retort 1 is preferably heated by a gas furnace or liquid fuel, and the whole or part of the waste gases from the same may be utilized for heating the separating pot or still 53, Fig. 11, which may be placed next to the retort.

The feed pipe 2 serving to conduct the mixture from the reservoir to the retort 1, as well as any other part of the plant which is liable to become clogged and thereby exposed to a dangerous pressure, may be provided with safety valves, as indicated at 38 in Fig. 1.

The retort is provided with one or two safety valves, to avoid any explosion by unexpected rise of pressure. The blow-off arrangements are so made, that the vapours will not escape to any dangerous part of the plant liable to cause fire or explosion, but are conducted to reservoirs or collecting chambers. The safety valve 38, Fig. 1, is adapted to blow off into a pipe 39, leading to the reservoir 28, and to operate at the same time an acoustic signal.

The safety device shown in Fig. 7 chiefly consists of a vertical tubular receptacle 39 containing authracene oil or [fol. 944] other liquid having a high boiling point. The said receptacle communicates with the retort 1 through a tube 40 situated above the level of the liquid, and with a high level reservoir 41 through an axial pipe 42, which has its inlet a short distance above the bottom of the receptacle 39. If the pressure of the vapours in the retort 1 is sufficient to overcome the hydrostatic pressure of the liquid in the receptacle 39, it will force the liquid into the high level reservoir and then escape. The liquid which has collected in the high level reservoir may be drawn off through a cock situated at the bottom of the same and then returned to the oil receptacle.

Instead of a vertical retort, as described, an inclined or horizontal retort containing a scraper or conveyor for conveying or scraping off and transporting the carbon may be employed, and the mechanical appliances for carrying out my process may be modified in other respects.

In Fig. 1 the intermediate tank 28 receives the pitch and oil mixture from a mixer 43 provided with an agitator 44, an outlet 45, and a heating furnace 46.

In Fig. 1, 26 represents the outlet for the vapours generated in the retort, and 27 is the pitch collecting pot, in

which the heavy oils are condensed and settle at the bottom, while the naphtha or other solvent vapours pass into a condenser 47. The liquid condensed in the coils of the latter, together with the uncondensed vapours, pass through an outlet 48 into a settling tank 49, which communicates through a pipe 50 with a collecting vessel 51.

The vapours arising from the latter (Fig. 11) are conducted through a pipe 52 into a second condenser 53, where they are wholly or partially condensed and then flow through the outlet 54 into an absorption tank 55, which contains liquids, such as cresote, capable of absorbing a portion of the solvent vapours led into the same. The remainder of the vapours and gases escape through a pipe 56 into one or more absorption tanks 57. A suction pump 59 communicates through the suction pipe 58 with the upper part of the last absorption tank 57, and promotes the flow of vapors through the condensers. Any vapours or gases which have not been absorbed are drawn into the pump and forced through the delivery pipe 97, to be burnt or otherwise utilised.

Instead of treating the tar as above described, I may distil it, until it approaches or attains the consistency of pitch, and then treat it as hereinafter described, that is to say, the pitch treated so as to maintain it in a liquid condition, or the tar, is mixed with a volatile solvent, such as benzine, [fol. 945] naphtha, or creosote, until the specific gravity of the mixture is below that of free carbon, in order to dissolve most of the viscous matter mixed with the same; then the carbon is allowed to settle from the mixture, and the supernatant liquid is drawn off, or a partial separation is produced by means of a centrifugal separator or filter or other mechanical means, and the concentrated carbon mixture thus obtained is forced into a filter-press provided with a washing appliance and a heating jacket, thereby forming press cakes, which may contain in addition to the free carbon some viscous or tarry matter holding the particles of carbon together.

Subsequently the oils or viscous matter contained in the cake is dissolved and driven out, by forcing naphtha or other volatile solvent through the filter press, so as to leave in the latter a mixture of free carbon and volatile solvent, after which the solvent is caused to evaporate by means of steam

or other heating fluid admitted to the heating jacket of the press, leaving behind the carbon in the shape of a very fine powder which may be used for the manufacture of electrodes without previous calcination, or may be mixed with lime or other suitable material for the manufacture of carbides.

Instead of driving out the solvent directly by heat it may be washed out by water, and the water afterwards evaporated by means of steam admitted to the heating jacket, or the solvent may be driven out by other known means.

Instead of subjecting the mixture of pitch or tar and light oils to a preliminary separation or concentration, as described above, it may be pumped into the filter press directly from the mixing vessel or still, or from an intermediate tank. The latter part of the solvent which has passed through the filter press for washing the carbon and is only slightly mixed with the heavier oils or impurities may be utilised for treating a fresh quantity of pitch or tar.

In the filter press plant represented by Figs. 13, 14, 15, 16, and 17, 60 is the mixing vessel and still to which tar is supplied from the receptacle 61 through a pipe 62, and solvent naphtha from the receptacle 63 through a pipe 64. The compressed air necessary for forcing the tar and naphtha out of the receptacles 61 and 63 is admitted through pipes 65 and 66. 67 is the driving shaft of the agitator mounted in the interior of the mixer.

The mixture of tar and solvent naphtha is drawn from the mixed 60 through a tap 68, by means of a suction pipe 69 and [fol. 946] pump 70, which forces the mixture through a delivery pipe 71 into a filter press 72.

The liquid which has passed through the filter press and has left its free carbon in the same, is let off through the pipe 73 to a still or to a boiler, and is then subjected to distillation so as to drive off the solvent, leaving behind a superior quality of pitch free from suspended carbon. The pipe 73 communicates also with the naphtha receptacles 63 and 74 through branch pipes 75 and 76, for the purpose hereafter described.

The vapors which are generated in the mixing vessel 60, when the tar is boiled down to the consistency of pitch, (or when the solvent is being mixed with the hot pitch, escape through pipe 77 into a condenser 78, which has an outlet box 79, communicating through pipe 80 with the receptacle 81 for lighter oils, and through pipe 82 with the receptacle 83

for heavier oils. 84 is a steam supply pipe, supplying steam to the mixer and still 60 and to the condenser 78 through branch pipes 85 and 86.

After the press cakes have been formed, and the supply of pitch or tar and naphtha mixture has been stopped, the press cakes are set in communication with the delivery pipe 87 of the pump 88, and the latter is made to draw solvent naphtha from the reservoir 63 through the suction pipe 89.

The first portion of the solvent naphtha, which has passed through the press, is allowed to escape through the outlet pipe 73 into a suitable receptacle (not shown); afterwards, that is to say, when the effluent from the press cakes is almost pure naphtha, it is diverted from the pipe 73, into the tank 63 or 74, in order to be used for a subsequent operation.

The construction of a filter press provided with a steam heating jacket is known, and need not be described in detail. In the drawing 90 indicates the steam pipe connected with the heating jacket, 91 a- airtight casing, which is provided with a liquid seal 92, so as to prevent the escape of vapour from the press. For driving out the washing naphtha from the press cakes or filter press compartments, the cake having been washed with naphtha, the steam pipe 90 is connected with the heating jacket of the press and the exhaust is allowed to escape through pipe 90^{11}. The naphtha vapours which are thereby produced in the press compartments escape through the pipe 93 into the condenser 94, and the liquid naphtha produced by condensation is allowed to run through the outlet 95 into the receptacle 96.

[fol. 947] If the raw material is the pitch-like residue resulting from the purification of petroleum or petroleum products with acid which contains finely divided carbon in suspension, and which residue has hitherto been useless or of little value, the said residue is first relieved of acid, before diluting it with light oils and subjecting it to the retort or filter press process, in order to separate the finely divided carbon from the asphalt-like material.

It will be evident, that in place of tar, pitch may be made the starting point; either the retort or filter press method may be used, the pitch being treated in a condition sufficiently hot to maintain it in a liquid state with volatile solvent. If it be desired to obtain free carbon by the distillation of petroleum or other oils which contain such free car-

bon in suspension, the distillation, is interrupted, when the residue in the still attains or approaches the consistency of pitch and is treated in the same manner as pitch, either by the retort or filter press process. In the manufacture of lubricating oils the distillation is interrupted at or before the residue has attained the consistency of pitch, and the residue is treated exactly as I have described in the treatment of tar. Instead of going to the dry distillation (making coke) I separate the residue into the liquid and solid constituents by diluting it with solvents and separate them either by heat or by the filter press process.

Where the purity of the carbon is the primary consideration, I interrupt the distillation of the tar or petroleum residue at any earlier stage, or I use the tar or petroleum residue without previous distillation, because I have found, that the further treatment of the tar or residue tends to charge the free carbon with impurity, which would have to be removed specially by washing acids or other means.

The process described above for separating oily residues into their solid and liquid constituents serves not only for extracting the suspended carbon, but also for removing other solid particles which may be suspended in the liquid and which reduce the value of the residue for the manufacture of lubricating oil, varnishes and other products.

The carbonaceous product obtained by my process has the shape of an exceedingly fine powder consisting of carbon mixed with a small quantity of volatile matter. Owing to its great purity and fine structure, the said powder may be used directly, that is to say without previous calcination, for the manufacture of arc lamp and other electrodes, but [fol. 948] in the manufacture of electrodes of great diameter it may occur that the calcination of the finished or moulded electrode would cause considerable contraction, in which case it may be necessary to calcine the fine carbon powder, so as to drive out most of the volatile matter, before the material is formed into electrodes.

Having now particularly described and ascertained the nature of my said invention, and in what manner the same is to be performed, I declare that what I claim is:

1. The improvement in the distillation of tar, which consists in first distilling off the light, and a portion of the heavy oils, until the consistency of pitch is approached or attained, then treating the residue with a volatile solvent,

separating free carbon from the mixture thus obtained, by means of mechanical pressure or heat, and obtaining a superior quality of pitch suitable for the manufacture of block fuel or varnish or for other industrial purposes.

2. The improvement in the treatment or utilisation of pitch, which consists in treating the same in a condition sufficiently heated to maintain it liquid, with volatile solvent, extracting the solid particles suspended in the liquid, and then subjecting the remainder to fractional distillation or fractional condensation, substantially as described.

3. In the treatment of tar or pitch, the extraction of carbon as an intermediate stage of operation, by means of a filter press or by aid of heat, substantially as described.

4. The process for obtaining carbon from tar, pitch or other viscous hydrocarbon mixture holding free carbon in suspension, which consists in mixing the said raw material with naphtha or other suitable solvent, separating out the free carbon by means of a filter press, washing out the tarry matter left in the press cakes by forcing solvent naphtha or other volatile solvent into the filter press and driving out the solvent by heat, as consecutive operations in the same filter press, substantially as described.

5. The process for obtaining carbon from a press cake produced from a mixturé of tar or pitch or petroleum residue and volatile solvents, which consists in forcing naphtha or other volatile solvent into the filter press containing the said press cake, then forcing out the solvent by means of water, and finally driving out the water by heat, substantially as described.

6. The utilization of the residue obtained by the chemical purification of petroleum by means of acid, which consists [fol. 949] in first removing the acid, then diluting the product with solvents, subsequently separating the free carbon from the mixture by means of heat or mechanical pressure, recovering the volatile solvents and converting the residue into asphalt, substantially as described.

7. The process for obtaining carbon by the distillation of petroleum, which consists in distilling the same until the

residue is of the consistency of pitch, treating such residue when in a sufficiently hot condition to remain liquid with volatile solvents and separating out the suspended solid particles by heat or mechanical pressure, substantially as described.

8. The process for obtaining carbon by the distillation of petroleum, which consists in distilling the same until the residue is of the nature of tar, then treating the residue with volatile solvents and separating carbon out of the residue so treated, substantially as described.

9. In apparatus for separating free carbon from a mixture of pitch and volatile solvent and free carbon, the combination of a retort with a reservoir for the said mixture exposed to pressure connected with the said retort by a feed pipe, a regulating valve inserted into the said feed pipe, an acoustic alarm device, and a float adapted to control the said regulating valve as well as the alarm device to indicate the level of the liquid in the reservoir, substantially as described.

10. In apparatus for separating free carbon from a mixture of pitch and volatile solvents with free carbon, the combination of a retort with an automatically adjustable scraper following the shape of the retort and adapted to revolve in the said retort, in order to scrape off the carbon deposited on the walls of the same, substantially as described.

11. In apparatus for separating free carbon from a mixture of pitch, volatile solvents and free carbon, the combination of a retort with an automatically adjustable scraper revolving in the said retort, a feed pipe connected with the reservoir for the said mixture and provided with a distributing nozzle, and a centrifugal governor geared together with the said scraper and adapted to control the flow of the said mixture through the said feed pipe, substantially as described.

12. In apparatus for separating free carbon from a mixture of pitch, volatile solvents and free carbon, the combination of a retort with a revolving scraper, a feed pipe adapted to supply said mixture to the retort through a distributing nozzle, a regulating tap inserted into the said [fol. 950] feed pipe, a flushing pipe adapted to supply steam

or oil under pressure to the said feed pipe or distributing nozzle, and a centrifugal governor geared together with the scraper shaft and adapted to control the regulating tap and the supply of steam or oil to the flushing pipe, substantially as described.

13. In apparatus for separating free carbon from a mixture of pitch, volatile solvents and free carbon the combination of a retort with a feed pipe provided with a regulating tap and a distributing nozzle, and a cooling jacket surrounding the said nozzle, substantially as described.

14. In apparatus for separating free carbon from a mixture of pitch, volatile solvents and free carbon, the combination of a retort provided with means for heating the same, with a feed pipe terminating in a distributing nozzle provided with a cooling jacket, a strainer situated in the upper part of the retort and adapted to intercept any solid particles carried off by the vapours on their way to the outlet, and a scavenging device adapted to supply steam or oil under pressure to the distributing nozzle and also to the strainer, substantially as described.

15. In the manufacture of carbon for electrodes or other purposes, the use of a carbonaceous raw material obtained substantially as described with or without previous calcination or other treatment as mentioned.

16. In the manufacture of calcium and other carbides the use of a carbonaceous raw material or mixture obtained substantially as described.

Dated this 28th., day of December 1901.

Fairfax & Wetter, Patent Agents, 37 & 39, Essex Street, Strand, London.

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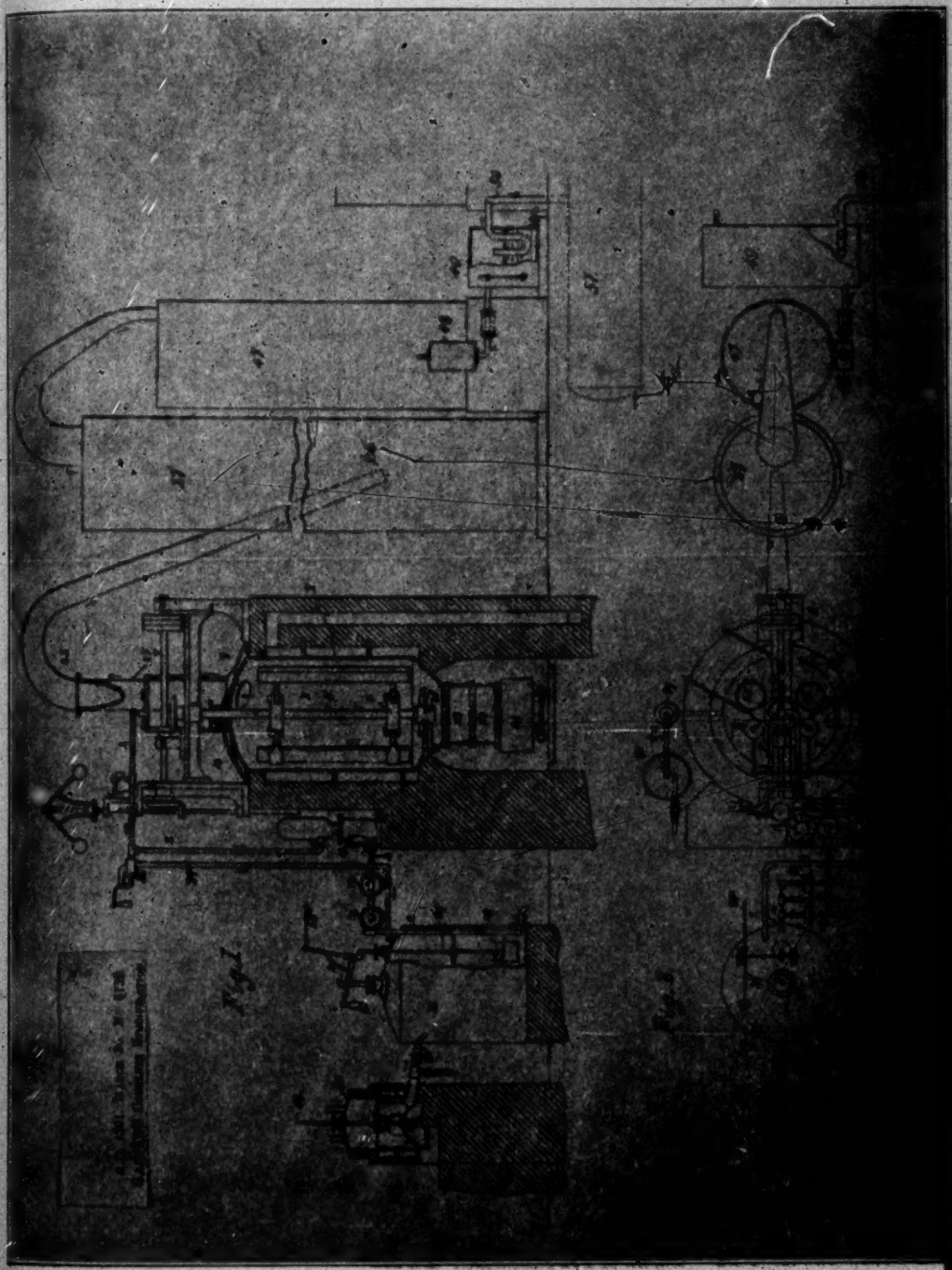
[fol. 951]



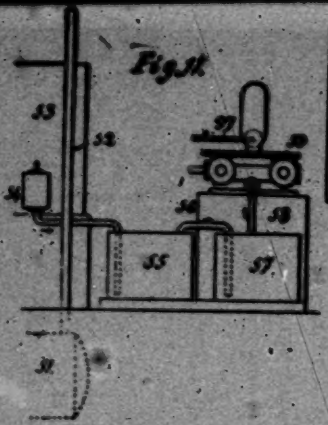


Fig.11.
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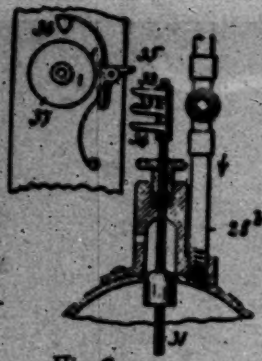
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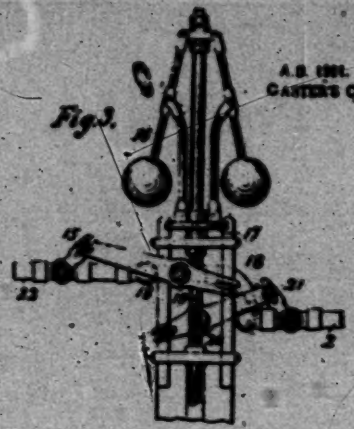
A.D. 1901. March 30. N° 6758.
CASTER'S Oxygen Generator.
Fig.3.
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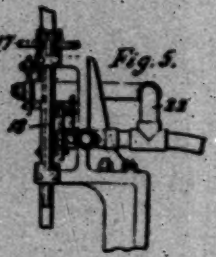
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Fig.5.
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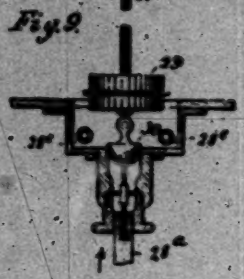
Fig.9.
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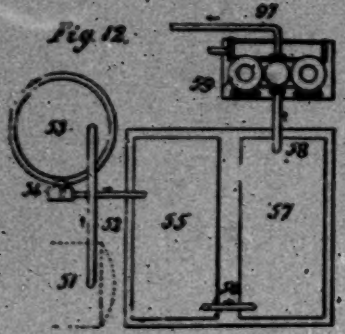
Fig.12.
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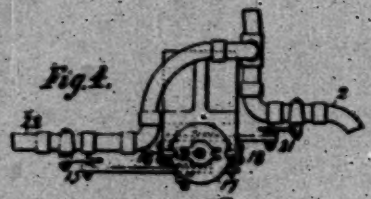
Fig.4.
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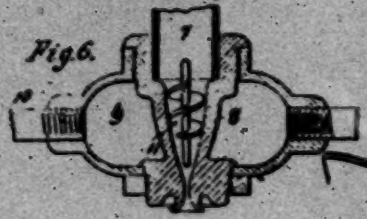
Fig.6.
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Fig.7
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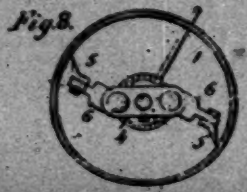
Fig.8.
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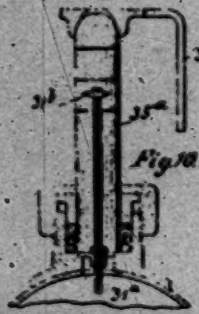
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Fig.10
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[fol. 953]

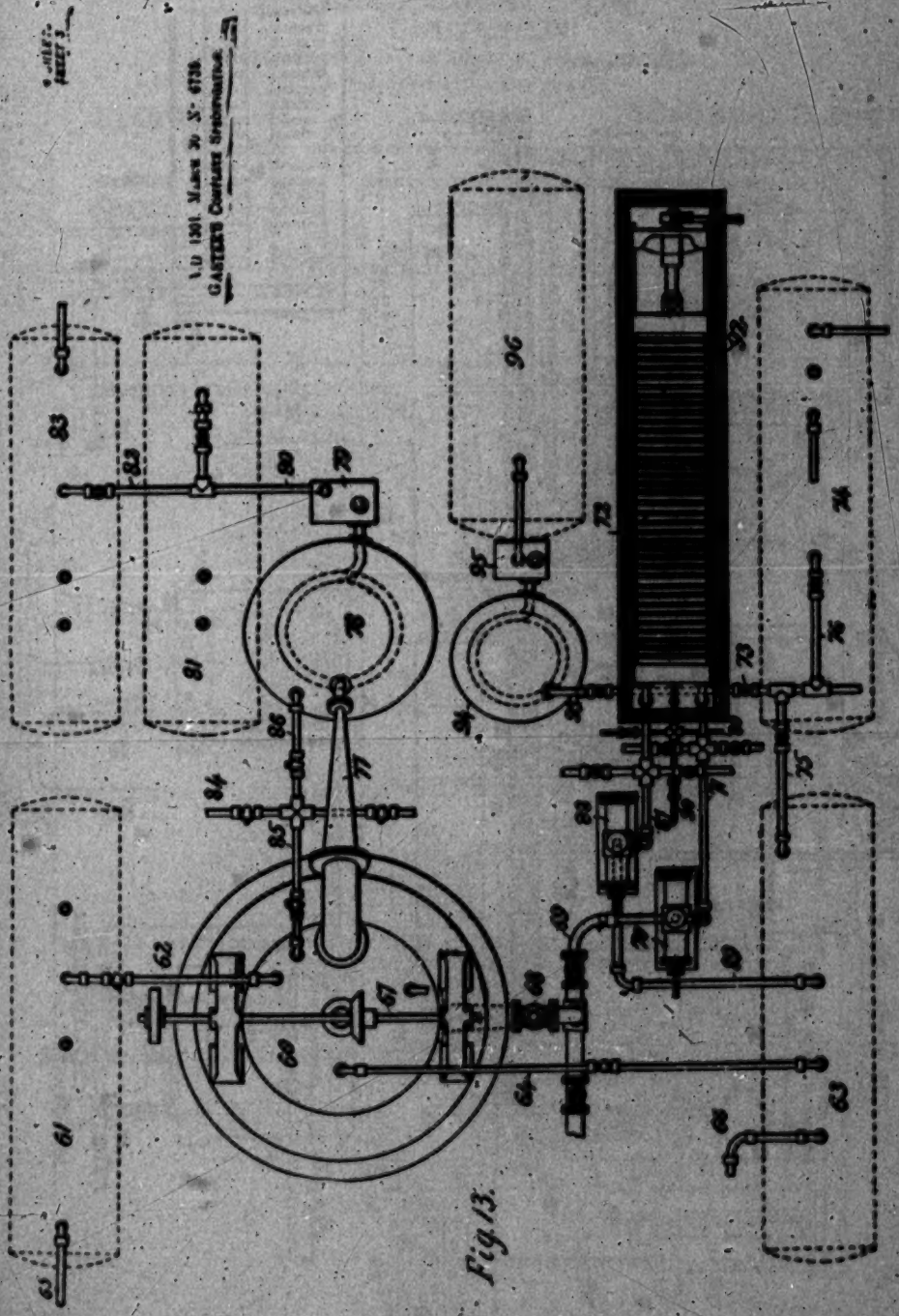


Fig. 13.

A.D. 1901 March 30. N° 6738.
GARRETT Continuous Rein-forcement.

Fig. 14.

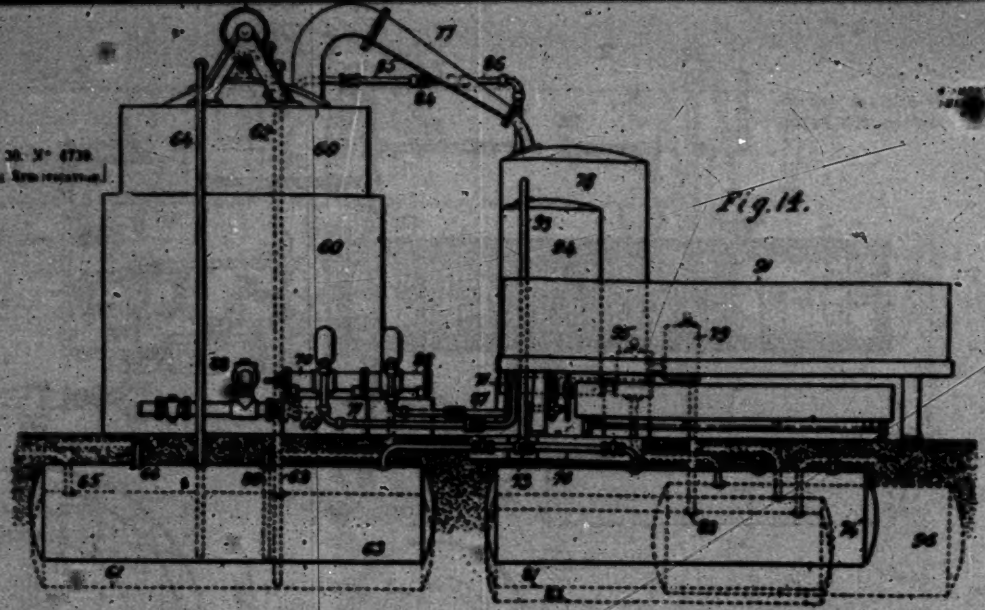


Fig. 17.

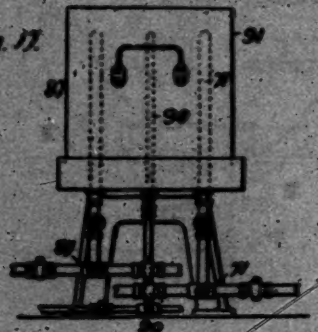


Fig. 16.

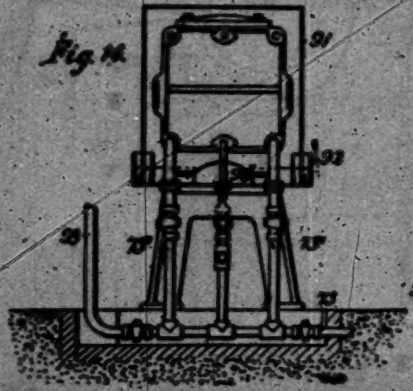
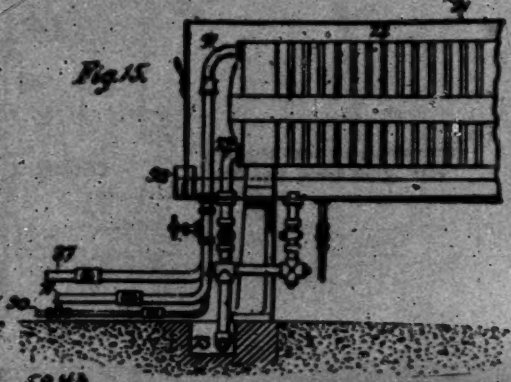


Fig. 15.



[fol. 955]

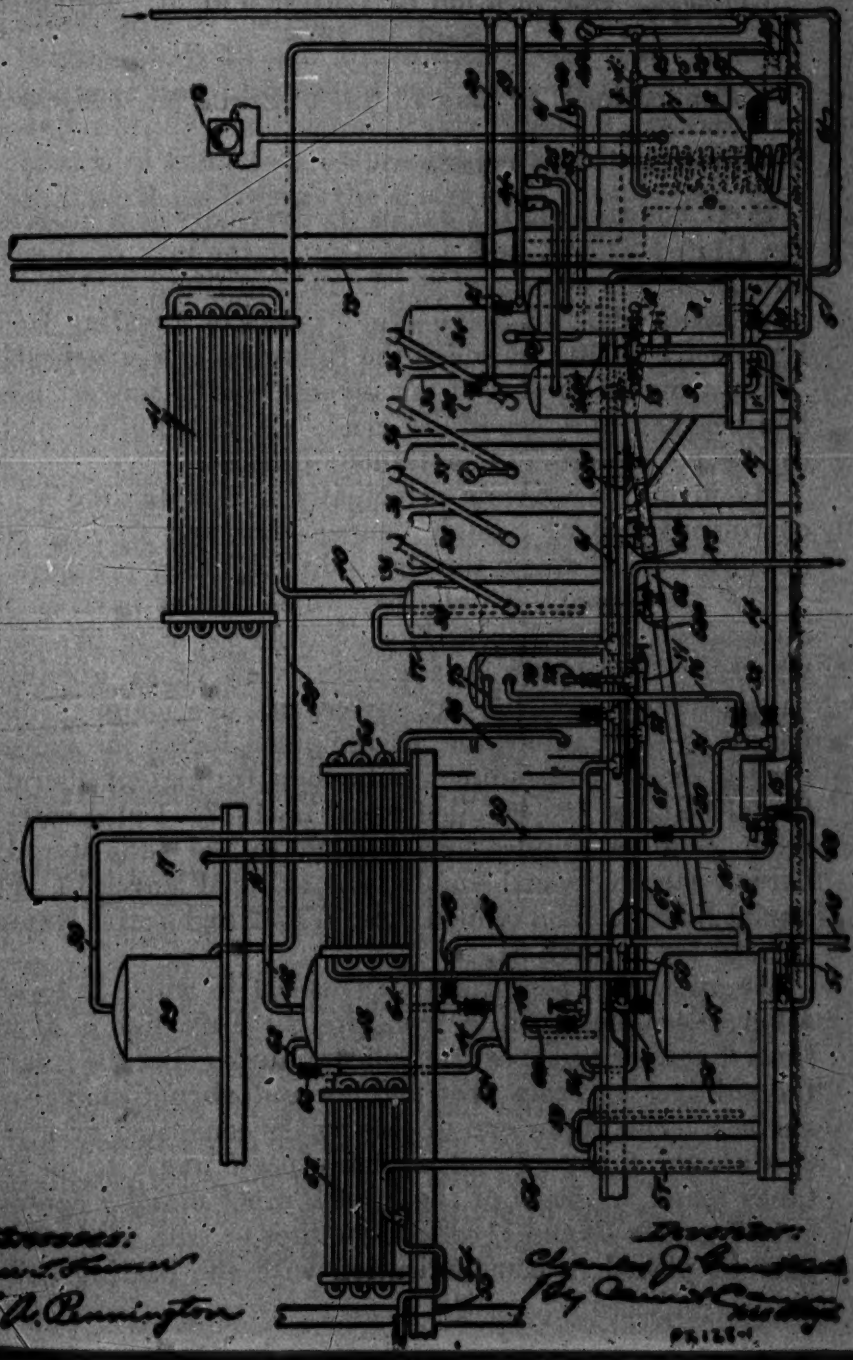
PETITIONER'S EXHIBIT 128

C. J. GREENSTREET.

PROCESS OF TREATING HEAVY HYDROCARBON OILS.

APPLICATION FILED MAY 15, 1913.

1,110,924. Patented Sept. 15, 1914.



Witnesses:
Geo. L. Fuller
F. A. Remington

Inventor:
Charles J. Greenstreet
By Cromwell & Cromwell
His Attys

PX 128-1

[fol. 956] United States Patent Office

Charles J. Greenstreet, of Webster Groves, Missouri

Process of Treating Heavy Hydrocarbon Oils

1,110,924. Specification of Letters Patent. Patented Sept. 15, 1914

Application filed May 13, 1912. Serial No. 696,891

To all whom it may concern:

Be it known that I, Charles J. Greenstreet, a citizen of the United States, and a resident of the city of Webster Groves, in the county of St. Louis and State of Missouri, have invented a new and useful Process of Treating Heavy Hydrocarbon Oils, of which the following is a specification.

The principal object of my invention is to convert heavy hydrocarbon oils, especially crude oil, into lighter hydrocarbon by a rapid and continuous process.

My invention consists principally in maintaining a long continuous coil at a high temperature and forcing commingled oil and steam through said coil under pressure.

The accompanying drawing, which forms part of this application, and wherein like symbols refer to like parts wherever they occur, is a general view of an apparatus suitable for practising my invention. No claim is made herein to such apparatus, as the same forms the subject-matter of my co-pending application for patent therefor, Serial Number 690,483 filed April 13, 1912. I also refer to other pending applications related to the subject-matter hereof, namely, Serial Number 614,125 filed March 13, 1911; Serial Number 702,176 filed June 7, 1912 and Serial Number 757,789 filed March 31, 1913.

My apparatus comprises a furnace 1 in which is located a long continuous coil of iron pipe 2. This pipe is of uniform diameter and free from abrupt angles, and the interior thereof is free from obstructions and abrupt changes of surface. The upper end of this coil is connected by a pipe 3, atomizer 4, pipe 5 and branch pipes 6 and 7 to oil feed tanks 8 and 9. Each of the branch pipes 6 and 7 contains cut off valves 10 and 11 whereby either or both of the tanks may be placed in communication with the heating coil 2,

as desired. The feed tanks 8 and 9 are likewise connected about midway of their height by valved branch pipes 12 and 13 with a pipe 14 which communicates with the delivery side of the pump 15; and the inlet side of said pump 15 communicates through a valved pipe 16 with an oil supply tank 17.

A steam pipe 18 leading from a boiler or source of steam has branch pipes 19 and 20 leading to the respective oil supply tanks 8 and 9, each of said pipes containing a control valve 21, 22; said supply tanks 8 and 9 are likewise provided with suitable pressure gages 23 and 24. Another branch pipe 25 leads from the steam pipe 18 and opens into the atomizer 4, whence it communicates through the pipe 3 with the heating coil 2; and this pipe 25 is likewise provided with a pressure gage 25'. Another branch pipe 26 leads from the steam pipe into suitable oil burner 27, which burner affords suitable means of heating the furnace. This oil burner is supplied with oil through a pipe 28 which communicates with an oil tank 29, this oil tank 29, in turn, communicates through a valved pipe 30 with a pipe 31 which communicates with the outlet pipe 14 of the pump 15 at a point between the pump and a valve 32 in said outlet pipe.

The outlet end of the heating coil 2 communicates through a pipe 33 with a condenser tank 34 about midway of the height thereof; and this condenser tank 34 communicates with a second condenser tank 35 through a pipe 36 extending from the top of the condenser tank 34 and opening into said tank 35 about midway of the height thereof. Likewise the tank 35 communicates with a third tank 37 and the third tank 37 with a fourth tank 38 and the fourth tank with a fifth tank 39, each tank in turn being connected to the next by the pipe 36 arranged as hereinbefore described.

The endmost tank 39 has a pipe 40 extending from the top thereof and communicating with a condensing coil 41 and said coil, in turn, communicates with the top of the tank 43 by means of a connecting pipe 42. This tank 43 is hereafter referred to as the gasolene separation tank.

The bottom of the gasolene tank 43 is provided with a valved pipe 44 which opens into the top of a tank 45 located immediately below the gasolene tank and hereinafter designated as a still tank; and the bottom of this still tank in turn connects through a valved pipe 46 with the top of a

tank 47, hereinafter referred to as the collection tank. A pipe 48 for drawing off the waste water connects through valved branches 49, 50 and 51 with the bottoms of the gasolene separation tank, still tank and collection tank, preferably, through the pipes 44 and 46 hereinbefore mentioned.

[fol. 957] Extending from the top of the still tank is a pipe 52 which communicates with a condensing coil 53; and the bottom of this coil is provided with a goose-neck or other suitable trap 54 in the delivery-pipe 55. Between the still and the trap is a pipe 56 which opens into the upper side of the delivery pipe and extends nearly to the bottom of a tank 57 which is partly filled with heavy oil and is hereinafter designated as the casing head gasolene tank. In practice, it is desirable to duplicate this casing head gasolene tank as shown at 58, the communication between the two pipes being made by means of a pipe 59 which extends from the top of the first casing head gasolene tank to near the bottom of the second tank.

The still tank 45 has a valved steam pipe 60 opening into the lower portion thereof. This steam pipe is connected to a pipe 61 which is a branch of the main steam pipe 18. The outlet pipe 52 of the still tank has a branch pipe 62 which communicates with the top of the gasoline tank 43, this branch pipe 62 containing a valve 63.

The collection tank 47 has an outlet pipe 64 extending from the top thereof to a reverse condenser 65 whose lower portion communicates with a tank 66. The bottom of said tank 66 communicates through a branch pipe with a pipe 67, which pipe in turn communicates with the valved pipe 46, which opens into the top of the collection tank. Opening into the lower portion of said collection tank 47 is a pipe 68 which has valved branches extending upwardly into the bottoms of the several condenser tanks 34, 35, 37, 38 and 39. The bottom of the collection tank 47 is provided with a valved pipe 69 which communicates with the inlet side of the pump 15.

A tank 70, hereinafter referred to as the supplemental supply tank, has a valved pipe 71 which communicates with the upper part of the collection tank 47 through the pipes 67 and 46. It also has a valved pipe 72 which communicates with an outlet pipe 73; and likewise the still tank 45 has a valved pipe 74 which communicates with the same

outlet pipe 73. Extending from the steam pipe 61 into the upper portion of the supplemental supply tank 70 is a valved branch pipe 75; and likewise a valved branch pipe 76 extends from the branch outlet pipe 31 of the pump and opens into the upper portion of said supplemental supply tank. By this arrangement, the supplemental supply tank can be readily replenished from the source of oil supply. A branch steam pipe 77 extending from the pipe 61 extends down through the last condenser tank 39 nearly to the bottom thereof and affords a means of heating and producing pressure on the contents thereof when it is desired to remove the same from said tank. Preferably, the furnace and the pressure gages and also the pyrometers 78 are all separated by a partition 79 from the other parts of the apparatus.

The operation of the apparatus is as follows: The furnace is first heated by means of the crude oil supplied from the feed tank 29 to the burner 27, where it is atomized by steam injected through the branch steam pipe 26. Meanwhile, steam from the branch pipe 25 is being injected through the atomizer 4 and forced through the apparatus under pressure from the original source of steam. During this preliminary heating not only the temperature of the coil is raised, but the temperature of the condensing tanks is also raised. When the heating coil reaches a cherry red heat, one or both of the valves in the branch steam pipes 19 and 20 are opened to produce a pressure on the crude oil supply tanks 8 and 9 or one of them; and either or both of the valves 10 and 11 in the outlet pipes of said tanks are opened gradually to permit the oil to be forced therefrom into the atomizer. The oil thus atomized is forced under the pressure of the steam through a long heating coil 2, where it is gradually transformed from heavier hydrocarbons into lighter hydrocarbons. This transformation is provided for and facilitated by the high temperature, the pressure inside of said coil, the continuous smoothness of the interior of the heating coil and the uniformity of its cross sectional area and by other factors incident to the apparatus.

The transformation of the heavy hydrocarbon compounds into lighter hydrocarbon compounds absorbs a considerable quantity of heat, and care must be taken to keep the temperature of the coil high enough to maintain the

continuity of the process. Although the whole coil may be a bright cherry red when the oil is first passed into it, the color of the inlet portion of said coil soon becomes dull on account of the rapid absorption of heat, even while the temperature of the furnace continues substantially uniform. Likewise, the transformation from a heavy hydrocarbon into lighter hydrocarbon implies an increase in the number of molecules and, consequently, an increase in the pressure within the heating coil by reason of the fact that the diameter of the heating coil is uniform throughout its length. Considerable pressure is therefore required to force the material through the heating coil rapidly. This pressure will increase as the length of the coil increases and its bore or internal diameter decreases. Satisfactory results are obtained when the heating coil is a continuous pipe with an inside diameter of about an inch and one-half [fol. 958] and of a length of one hundred feet, when the initial stream pressure is one-hundred pounds per square inch, and the pressure on the oil in the feed tank is about fifty pounds per square inch, the temperature being cherry red as above stated.

It is to be noted that the temperature of the heating coil influences the products, but that the products which result from the treatment of given crude oil at a given temperature are of a definite and uniform quality. For instance, certain definite and uniform products can be obtained from a given crude oil by treating the same at a red heat; whereas certain other products also of a definite and uniform quality will be obtained by treating another portion of the same crude oil at a bright cherry heat. The temperature may be varied therefor to suit the requirements of the desired product. The product resulting from the foregoing treatment is a mixture consisting principally of paraffins and olefins, the amount of olefins varying from a small percentage in the lighter gasolenes and naphthas to as high as forty per cent. or more in the heavier oils. The product is free from grease and is therefore suitable for cleansing purposes and for use in internal combustion motors, as well as for all the purposes for which ordinary gasolene and naphtha are used. On account of its large content of olefin, the gasolene produced by my process has a higher heating efficiency than gasolene produced by the processes commonly practiced.

As a matter of economy, it is desirable to limit the quantity of steam or water used in the process; and for determining the proper quantity of water and steam, a test burner 80 is used. This test burner is connected by a pipe 81 to the delivery pipe 33 of the heating coil 2. Initially steam alone will issue from the test burner; but when the crude oil is admitted in gradually increasing quantity, the vapor resulting therefrom will issue along with the steam through the test burner. So long as the steam is largely in excess, the vapor issuing from the test burner will not burn with a steady flame; and consequently, the oil should be admitted in larger proportion to the atomizer until the vapor issuing from the test burner burns with a continuous flame. The test burner should be of the Bunsen type so as to insure a thorough commingling of air with the vapor before ignition. The proportion of oil can be increased until the test flame shows a tendency to a reddish or yellowish color, which color indicates a destruction of a portion of the oil. When this color indication appears, the proportion of oil should be slightly decreased until the test flame becomes bluish.

From the heating coil, the product passes into the first condensing tank, where the more easily condensable portion of the product is condensed. The remainder of the product passes into the next tank where the more easily condensable portion thereof is condensed, and so on from tank to tank. As the operation of the apparatus continues the condenser tanks gradually become hotter, so that a portion of the product which condenses in a given tank in the early period of the operation will distil over to the next tank at a later period of the operation. It is desirable to continue the operation until the temperature of the last condensing tank is slightly in excess of the boiling point of water.

From the last condensing tank, the product passes through the condensing coil 41, which is preferably cooled by water or other artificial means; so that the resulting product which enters the gasolene tank is mostly gasolene and water. The water being heavier than the oil is drawn out from time to time from the bottom of the gasolene tank 43 through the waste pipe 49; and the gasolene is then passed through the pipe 44 into a still tank 45, whereupon the connection between the gasolene tank and still tank is

cut off. Live steam is then injected through the branch pipe 60 into the still tank with the result of vaporizing the lighter portion of the contents of the still tank, which lighter portion passes out through the pipe 52 into the condensing coil 53. From the condensing coil the gasolene passes to the delivery pipe 55; but the lightest portion of the gasolene is trapped and escapes through the by-pass 56 into the casing head gasolene tank 57 where it is absorbed by the heavy oil provided for the purpose in said tank. After this distillation the operation is continued for some time, the water in the still tank is drawn off and the remaining contents are passed into the collection tank 47. From time to time the contents of one or more of the condenser tanks is drained into this collection tank and as the temperature of the contents of the condenser tanks is high, a portion thereof will evaporate and pass through the reverse condenser whence it is returned when desired to the collction tank. When desired, the communication between the supplemental supply tank and the collection tank is opened to allow crude oil to be forced into the collection tank, the collection tank thus receives a portion of the product condensed in the condensing tanks as well as the residue of the still tank and a portion of crude oil. The collection tank is placed in communication with the supply pipe of the pump either alone or simultaneously with the main-supply tank, as desired; so that the contents of said collection tank are passed through the apparatus in the same way as the original supply of crude oil.

[fol. 959] In the operation of my apparatus, the innner surface of the heating coil soon becomes covered with an enamel or very smooth coating of magnetic iron-oxide; and on account of the smoothness of this coating, it is believed to contribute to the value of the process in increasing the velocity of the contents and by not affording any point where a deposit of carbon may be made. When the process is properly carried out, there is practically no formation of permanent gas and no deposit of free carbon; and as the condensable vapors condense in the condensing tanks, the last of which has a vent to permit the escape of the air initially contained therein, the pressure in the condensing tanks decreases from tank to tank until it is about the same as that of the surrounding atmosphere.

What I claim as my invention and desire to secure by Letters Patent is:

1. The improvement in the process of treating crude oil which consists in passing steam under pressure through a long continuous coil of pipe kept at a substantially cherry temperature and injecting crude oil into said steam on the inlet side of the coil, said coil being free from obstructions and abrupt angles.

2. The improvement in the process of treating crude oil which consists in passing a continuous current of commingled steam and oil through a long continuous coil of pipe kept at a substantially cherry red temperature, said current being unobstructed and moving at a velocity rapid enough to prevent a deposit of carbon or formation of permanent gas in appreciable quantity such as would result from the prolonged exposure of the oil at such temperature.

3. The process of treating crude oil which consists of forcing a stream of commingled steam and oil through a long continuous coil of pipe kept at a substantially cherry red temperature, the exposure of the oil being such as would result from the use of a coil of pipe one hundred feet long and an inch and a half diameter and free from obstructions, the pressure on the oil supply being fifty pounds per square inch, such oil being injected into the pipe coil under a steam pressure of one hundred pounds per square inch.

4. The process of treating crude oil which consists in maintaining a long coil of continuous pipe at a substantially cherry red temperature, passing steam through said coil in a continuous and unobstructed stream, injecting oil into the stream on the inlet side of said coil and condensing the oil beyond the outlet end of said coil, the exposure of the oil being such as would result from a live steam pressure of one hundred pounds per square inch and a pressure on the oil supply of fifty pounds per square inch when the coil is a pipe of one and one-half inches in diameter and one hundred feet long.

5. The process of treating heavy hydrocarbon oil which consists in maintaining a long coil of continuous pipe at a substantially cherry red temperature, passing steam through said coil in a continuous and unobstructed st-eam, injecting oil into the steam on the inlet side of said coil and condens-

ing the oil beyond the outlet end of said coil, the exposure of the oil being such as would result from a live steam pressure of one hundred pounds per square inch and a pressure on the oil supply of fifty pounds per square inch when the coil is a pipe of one and one-half inch diameter and one hundred feet long.

6. The process of treating crude oil which consists in maintaining a long coil of uniform small diamcter at a temperature sufficient to decompose the principal components of the crude oil, passing steam through said coil in a continuous unobstructed current, injecting oil into said steam on the inlet side of said coil and permitting the products to condense beyond the outlet end of said coil.

7. The process of treating crude oil which consists in passing steam through a long unobstructed pipe of small diameter and free from abrupt angles at a temperature sufficient to transform some of the heavy hydrocarbon ingredients of crude oil into lighter liquid hydrocarbons and simultaneously injecting crude oil into said steam on the inlet side of said coil, and permitting the product to condense, the pressure on the oil and the pressure of the steam at the point of admission to said pipe being sufficient to produce a rapid velocity through the coil.

8. The process of treating heavy hydrocarbon oils which consists in passing steam through a long unobstructed pipe of small diameter and free from abrupt angles at a temperature sufficient to decompose some of the ingredients of said oil and simultaneously injecting the oil into said steam on the inlet side of said coil, and permitting the product to condense, the pressure on the oil and the pressure of the steam at the point of admission to said pipe being sufficient to force the oil rapidly through the coil.

9. In the art of treating crude hydrocarbon oil with steam at a temperature in excess of the distillation points of the heavy hydrocarbon components thereof, the method of determining the amount of the steam, which consists in igniting a portion of the issuing vapor and gradually changing the proportion of oil until the test flame becomes yellowish and then slightly decreasing the proportion of oil.

[fol. 960] 10. The process of treating crude oil which consists in passing a mixture of said oil and steam through a

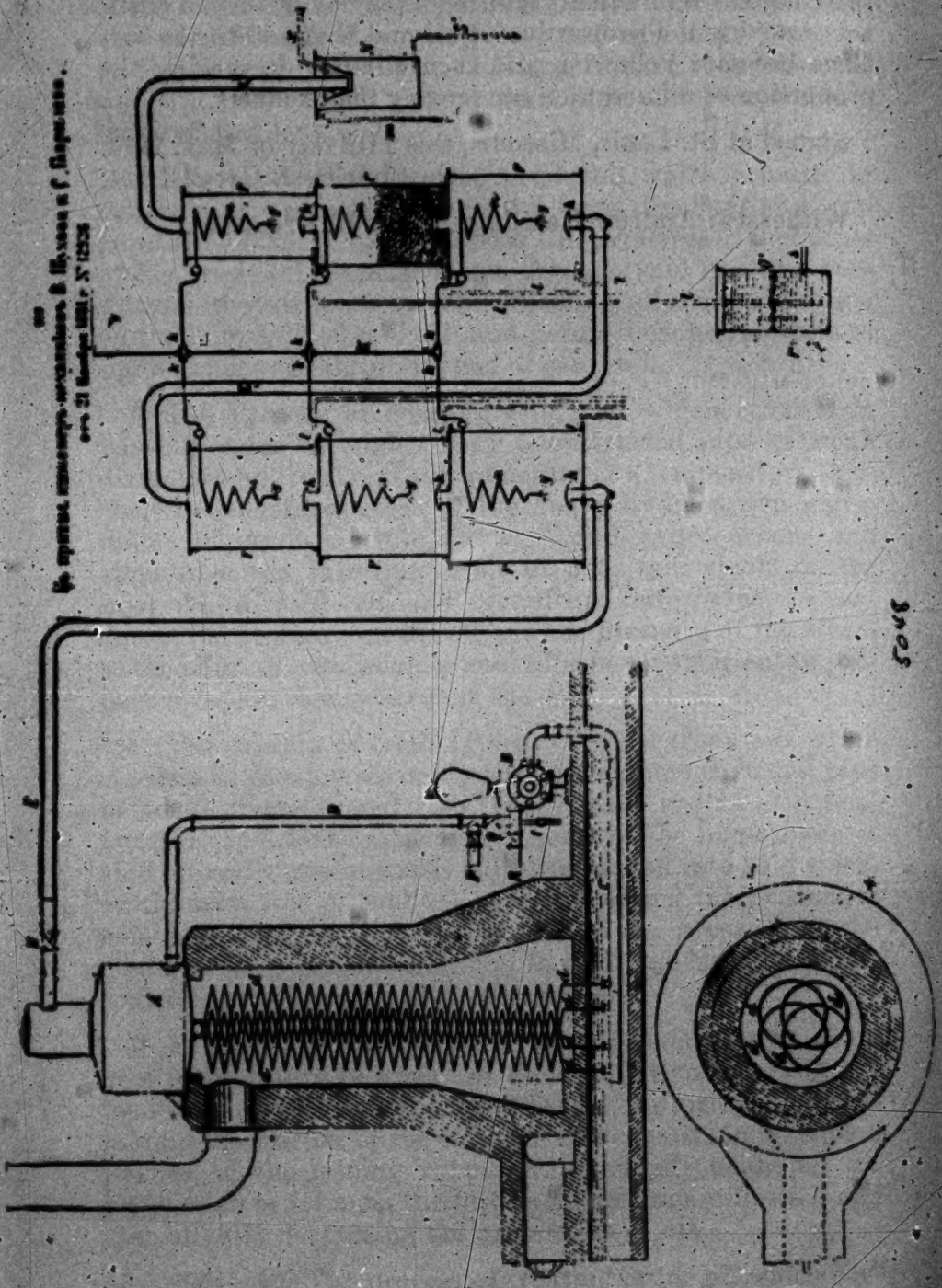
heating coil at a furnace temperature in excess of one thousand degrees Fahrenheit; igniting a portion of the hot products, varying the proportion of oil and steam until the test flame becomes yellowish and then slightly decreasing the proportion of oil and then condensing the products.

Signed at St. Louis, Missouri, this 11th day of May, 1912.

Charles J. Greenstreet.

Witnesses: Andrew Kessling, Albert H. Croissant.

[fol. 961] PETITIONER'S EXHIBIT No. 129



[fol. 962] TRANSLATION OF PETITIONER'S EXHIBIT No. 129

(Russian) 175

Patents granted by the Department of Commerce and Manufacturers in 1891 to the mechanical engineers Vladimir Schukhov and Sergyey Gavrilov for machinery for the continuous fractional distillation of petroleum and similar liquids and also for the continuous recovery of *of* gas from petroleum and its products

The Engineer technologist Kaupe and the technologist of the 1st class Chokalov, on January 24, 1890, entered the Department of Commerce and Manufacturers with the request that there be given to the mechanical engineers Vladimir Schukhov and Sergyey Gavrilov who live in Moscow, ten years patents on machinery for the continuous fractional distillation of petroleum and other liquids, and also for the continuous recovery of gas from petroleum and its products.

The object of the invention is the machinery which is represented in the plan for the continuous fractional distillation of petroleum and other liquids, and also for the recovery of gas from petroleum and its products.

Petroleum or its residues, flowing into the opening R of the pump B is taken up with this pump and under considerable pressure is forced through the pipe C into the coils, *d*, *d*, *d*, * * *, which are subjected to the action of the hot gases of the furnace, into which they are cemented. In these coils the liquid, being put in them by the action of the pump, is heated to a high temperature and dependent upon the dimensions of the pipes of the coils and the speed at which the pump is operated, it is subjected either to the process of distillation or to the process of decomposition, in addition to which the process under which the process is carried on, is regulated by the cocks M and P, as will be shown later. The construction of the coils may vary and they may be replaced by straight pipes. The mixture of gases, vapors, distillates and residue liquid which is formed in the coils, passes into the cylindrical vessel A, in which the liquid settles to the bottom, while the gases and vapors [fol. 963] pass, through pipe E, to the separators of the

distilled products and the coolers. For the better separation of the liquid from the gas and the vapors, the cylinder A is filled with any crushed material, e. g., pieces of cast-iron, coke, etc. According to the rapidity of the circulation of the liquid in the pipes and dependent upon the object of the distillation, the liquid settling in the cylinder A, is let out through the pipe D and through the cock P, without being submitted to further distillation, or else by the aid of the cock Q, it again enters the pump where it is mixed with the fresh liquid flowing into the pump and passes in further circulation through the coils. In this way, by means of the cocks P and Q, there is secured a greater or lesser degree of the repeated process of circulation and of the connected distillation or decomposition of the liquids. Independent of the flow of the liquid which is being distilled into the pump through the cock R, part of the liquid which is being distilled can be admitted directly into the cylinder A, for the dephlegmation of the vapors formed in the coils. In the distillation of high boilings kinds of petroleum and residues, there may be introduced into the opening of the pump which received the petroleum, through the cock *t* light petroleum products, as benzine and gasoline, which are mixed at the pump B with the liquid which is being distilled and which pass with it into the coils for the corresponding process of distillation. The structure which has been described renders it possible, with a comparatively small expenditure of materials for the construction of the heating surfaces in the distilling apparatus, to distill or decompose a considerable amount of liquids, in addition to which through the action of the circulation pump there are removed all wastes and coke-like deposits which are formed during the process of distillation and decomposition. The products in the forms of vapors and gases pass from the cylinder A, through the pipe E, into a series of separators of the distilled products and coolers. The separators for the distilled products consists of an arbitrary number (according to the number of the products which are being recovered of cylinders F, arbitrarily placed but so connected with one another that the vapors of the products pass each time into the lower part of the cylinder and pass out from its upper part. On the plan there is represented a case where six cylinders are placed in two columns. In

each of the cylinders F the vapors and gases pass through the opening H and are cooled by a liquid which is admitted through the pipe K, *k* and the coil *n*. The liquid flows into [fol. 964] the mass of vapors in small streams through the opening of the head *v*. The moisture, admitted to cool the products, has a lower boiling point than the vapors of the liquid for the condensation of which the cylinder is destined. Thus, for example, in the case of kerosine, which boils at more than 100 degrees the liquid admitted through the coil *n* will be water, which by its turning into vapor takes away the latent heat of the vapors of kerosene, whereby one pound of water which is spurted in, will condense about eight pounds of kerosene; the water vapors which are formed pass with the remaining vapors of kerosene into the next cylinder, where this mixture will be subjected to further condensation of the vapors of kerosene with the addition of water vapors. The vapors which are not condensed in the battery of cylinders F, pass along with the water vapors from the last cylinder through the pipe E^2 into the vessel N, where by means of a conical cap and the action of a stream of water admitted by the pipe X, they are finally condensed, in which process the products with less specific gravity than water, are removed through the pipe *m*, and the water through the pipe S^1. For the more successful operation of these separators of the distilled products which have been described, the interior of each of these is filled with crushed material S placed within the cylinder. The vapors of the material which is being distilled, when turned into a liquid, are removed in a hot state from the cylinders through the pipe 1, 1 and enter the compartment Q^1 through which water is continuously flowing. In these compartments the hot liquid, being mixed with water, is cooled to the needed temperature and since it is of less specific gravity than water, the cooled products because of the slow movement of the water and the large size of the compartment are easily separated and taken from the vessels through the pipes *r*. The Specific gravity of the condensed products recovered in the cylinders F, is strictly determined by the amount of water admitted into these cylinders by the coil. Thanks to the above described apparatus, there is shown the possibility to cool in a comparatively small space and to divide

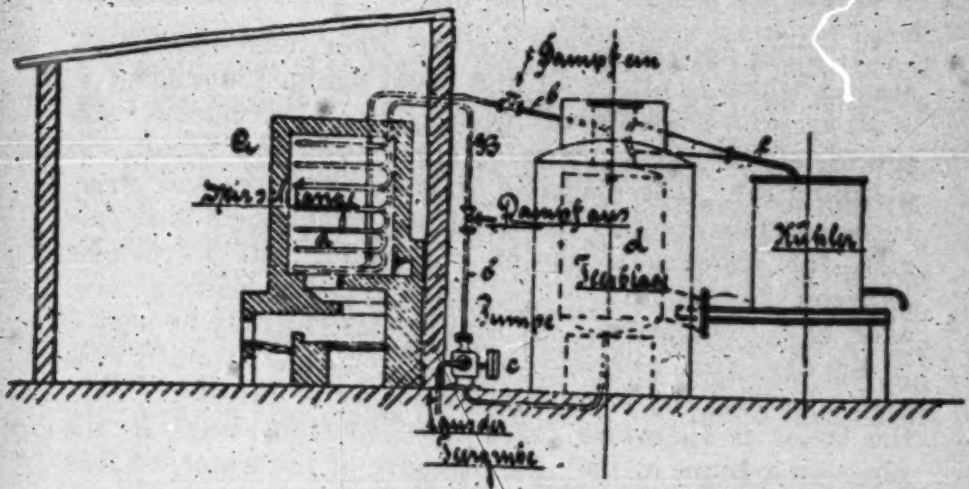
the products of a large quantity of liquid which is being distilled, since the same apparatus permits us to replace the commonly used metallic cooling surfaces with a direct contact between the cooling medium and the vapors of distillation. Besides this the use — such separators for the distilled products permits the rigorous establishment of the exact specific gravity of the products which are being recovered and which are the object of the distillation. [fol. 965] After the consideration of this invention in the Ministry of Commerce and Manufacturers, the Minister of Finance, on the basis of Art. 188, Statutes of Commerce, Collected Laws, Vol. XI, edition of 1887, warning that the Government does not vouch for the actual ownership of the invention by the applicants nor for the success of the same, and affirming that no patent has been previously given in Russia to any other person for this invention, gives to the mechanical engineers Vladimir Schukhov and Sergyey Gavrilov this patent for ten years from the annexed date with exclusive rights to the above described invention, according to the description and plan which have been submitted, in the entire Russian Empire to use, sell, bestow, publish and in any other way yield to anyone else in lawful manner, but with the condition that this invention according to Art. 191 of the same Code be put into full operation not later than at the expiration of one quarter of the time allotted for the life of the patent, and that thereafter within six months there be presented to the Department of Commerce and Manufacturers the certification of the local authorities to the fact that the patent has been placed in actual operation, i.e., that the patented invention is brought into use; otherwise this right, on the basis of Art. 197, is abrogated. The tax of 450 rubles has been paid; in token whereof this patent is signed by the Minister of Finance and confirmed by the seal of the Department of Commerce and Manufacturers.

St. Petersburg, November 27, 1981.

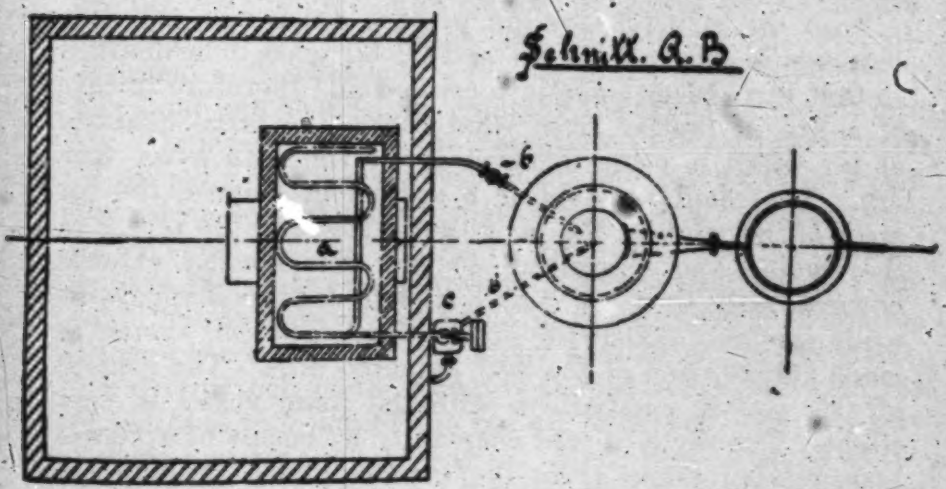
Translation made by Clarence A. Manning, Asst. Prof. of Slavonic languages, Columbia University.

[fol. 966] PETITIONER'S EXHIBIT No. 130

Aufriss.



Schnitt A. B



Zu der Patentschrift

№ 166723.

PHOTOGR. DRUCK DER REICHSDRUCKEREI

[fol. 967] TRANSLATION OF PETITIONER'S EXHIBIT No. 130

Translation of German Patent No. 166723 to de Clerq Patent Gesellschaft zur Fabrikation von Teer-under Dachpappen—Machinen m.b. H., in force Jan. 27, 1904, published Jan. 10, 1906.

Distilling apparatus for tar and other inflammable substances which is fire-proof and proof again- foaming over.

Many tests have already been made and structures completed, all for the purpose of eliminating fire hazards in distilling tar. The principle of these processes and structures consisted mainly in that a non-combustible heat carrier, for instance steam or hot water, was introduced between the tar and the fire. Both types of heating, however, have the disadvantage that the tar can only be heated to 400 deg., but in practice only 150 deg. was attained with steam heating and 200 deg. with hot water heating. With the latter temperature there were constant leaks in the pipes on account of the high pressure of the water, so that frequent repairs were necessary. It is, therefore, easily und-rstood that both processes have not found general employment.

With the structure of the present apparatus, the procedure is to separate the fire and the tar mass to be distilled so that they never come into contact and therefore in case of a fire no matter from what cause, the large quantity of tar which is being distilled at the time can never take fire. The plant consists of a system of coils *a*, the tar main *b*, the pump *c*, the tar receptacle *d* and the pipe *e* to the cooling and separating device. The novelty extends however only to *a b c d* as complete distilling apparatus while *e* is only added for illustration. The coil system is made vertical and of the best patented pipe. The content of this coil in comparison with the foam vessel is very slight. The tar is forced constantly by means of a simple transmission pump from the tar receptacle through the coil system in the fire, and after heating it goes back to the receptacle where it gives off the gases which go to the cooler, the liquid continuing to circulate and being gradually distilled down to the desired temperature.

The pump which keeps the tar constantly in circulation is so arranged between receptacle and coil system that the [fol. 968] liquid is first forced to flow constantly to the

pump as the latter is situated lower than the receptacle and secondly the liquid can never flow into the coil system when the pump is not in operation, since the pump when at rest closes the main and the pressure pipe to the coil system extends highest than the highest tar level. The furnace is separated from the rest of the distilling apparatus by fireproof walls in such a way that the flame can never reach the main mass of the tar. The coil system is so constructed that the receptacle can be easily cleaned and the separate parts easily and rapidly cleaned.

The tar receptacle differs in general very little from those used heretofore. It is entirely insulated so that the warm liquid gives off as little heat as possible, it has a thermometer which operates in the known way, a testing cock for filling and an outlet opening in the bottom, which makes it possible to use the vessel as pitch cooler at the same time. After completed sistillation, the pitch can run off directly into molds or receptacles by simple turning of a cock.

The pump is driven by the transmission or by steam pistons, by means of conical belt pulleys, so that by shifting the belt guide or the steam valve by a single hand operation the tar can circulate more rapidly or slowly during the distillation or the circulation can be interrupted. By adjustment of T-cocks before the beginning of the distillation, the pump can be used for pumping the tar from the pit into the receptacle. After the receptacle is filled, the T-cock is turned, the coils are heated up and the pump is again turned on so that the distillation can begin. After a very short time, the tar begins to give off steam and benzol vapors and quite energetically. The fire need not be regulated but as soon as the liquid in the receptacle foams up, as happens very often with direct heating of the receptacle, the driving belt of the pump is shifted somewhat until the speed of circulation of the hot air is correct. In this way foaming over no longer occurs. Much time is saved as the great heat of the heating system rapidly expels the water from the tar. When the operator no longer hears the characteristic noise of steam in the receptacle, he knows that the tar has given off all of its water. He now runs the pump at full speed and the distillation proceeds.

The furnace is an insulated chamber so that in case a heating coil burns through, the tar from the coil flows over

the fire in a pit. This pit is situated inside the heating building so that if this burning liquid can not be dis- [fol. 969] tingushed, the fire always remains confined to the pit in the building. The quantity of the liquid in the pit is very small and therefore in case of a fire soon burns out since new tar is not supplied to it, the fireman as soon as he notices the tar flowing into the fire having turned off the pump. Assuming that the a tar in the small pit has entirely burned out, a substitute pipe inserted a few hours after cooling of the furnace and the apparatus is again ready for use.

In way of comparison it may be mentioned that the process of heating the tar in a single operation without interruption to the final temperature is already known. However on account of the great quantity of gas formed continuously, the apparatus requires a comparatively large pipe coil closed at both ends.

Moreover with this process there is more danger of fire than with the process according to the invention since the great quantity of tar present in the superheater is naturally under great pressure and upon leaks in the coil a much greater spreading of the burning quantity may be expected.

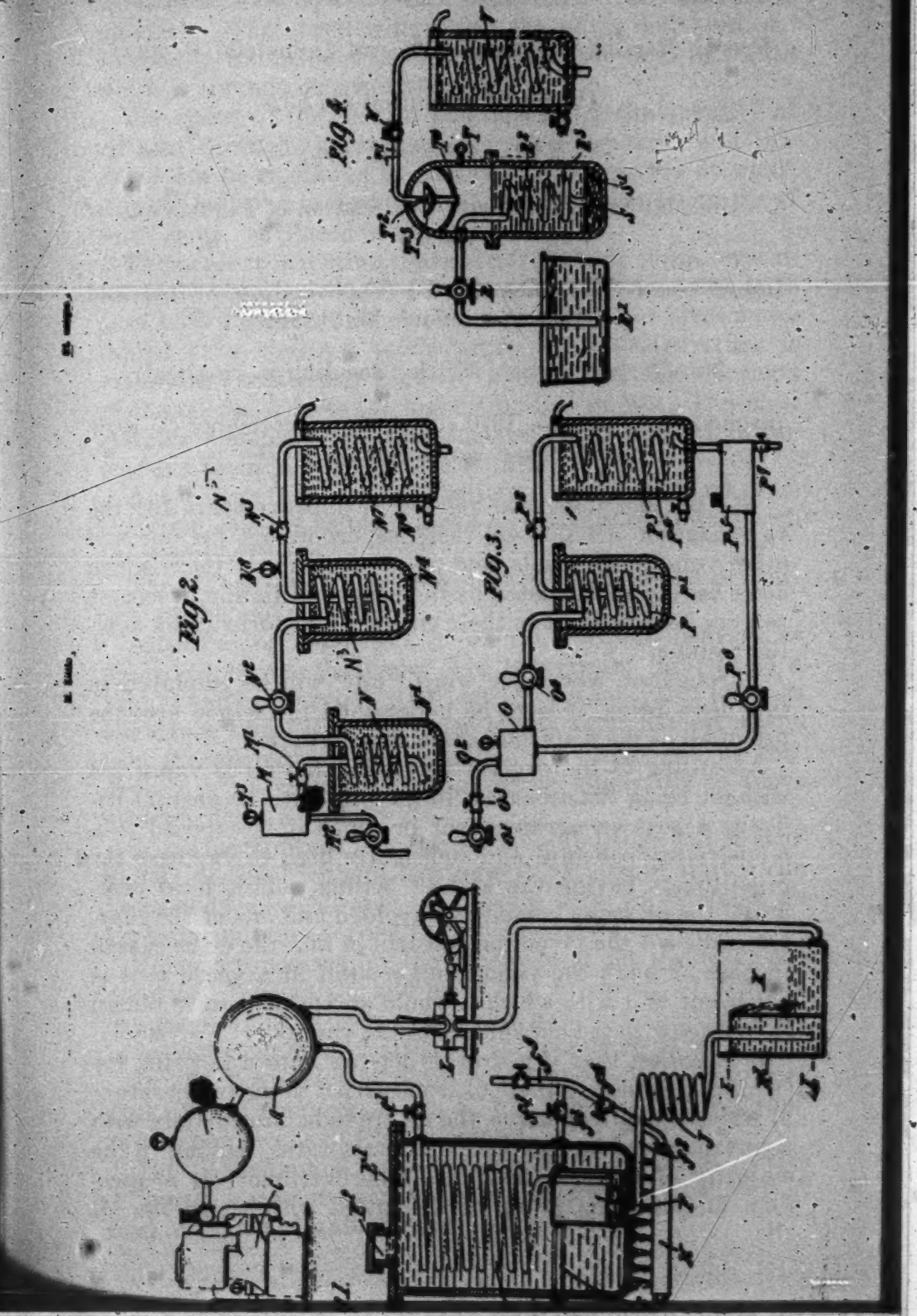
The known device for distilling liquids, which with increasing temperature give off different fractions successively, is not suitable for the present purpose, since the means there provided for maintaining circulation of the liquid (great quantity of liquid) is not sufficient with liquids such as tar for producing a regular constant circulation of the liquid, which can be accomplished only by a mechanical supply means (pump).

Claim

Distilling apparatus for tar and other inflammable substances which is fire-proof and free from foaming over, characterized in that a heating coil system, a closed receptacle and a pump are so connected by pipes that not the whole amount of liquid to be distilled but only the charge of the heating coil can come into direct contact with the fire and the liquid be distilled is set into circulation by the pump so that upon heating of the heating system there is distillation of the tar.

Tr. MMJ.
6-11-25.

[fol. 970] PETITIONER'S EXHIBIT No. 131



[fol. 971] TRANSLATION OF PETITIONER'S EXHIBIT No. 131

French Republic, National Office of Industrial Property

Patent of Invention 417,532

XIV.—Chemical Arts

6.—Distillation—Filtration—Purification of Liquids and of Gases

Improvements Relating to the Vaporization of Oil and Other Analogous Materials

Mr. Herbert Arnold Kittle, Residing in England

Applied for June 25, 1910. Patented September 2, 1910.
Published November 16, 1910

The present invention relates to improvements for the vaporization of oil, of oil residues, crude oils, tar oils and other volatile materials, and more particularly those which after having been treated by the usual distillation processes can not be vaporized in their entirety and form a non volatile residue.

Throughout, where the word "oil" will be employed in this description, it is to be understood to include also the use of all of the materials enumerated above.

According to the present invention, the oil is vaporized without being fractionated, in passing with a constant delivery across an arrangement in which it is exposed to a temperature constant and sufficiently high to vaporize the constituents having the highest boiling points, local heating of the oil being completely avoided and one of the characteristics of the invention consists in that the oil is caused to pass through the vaporizing conduit at a speed that is not below that with which it would spread if it were placed in contact with the hot surface of the vaporizer.

It is known that if a drop is let fall onto a hot tile, for [fol. 972] instance a plate of iron carried to the temperature at which the oil vaporizes, the oil spreads immediately with a certain speed on the plate and evaporates, leaving in the majority of cases, a residue. Wherever there is a question, in this description, of the speed with which the oil

spreads, it is the speed which comes to be described that is intended. The speed with which the oil is delivered, according to the present invention, is greater than that with which it spreads on a hot plate.

The speed of the current will depend on the quantity of oil sent through the apparatus in a given time, and this speed can be regulated by means of the pressure at which it is caused to pass through the apparatus and by means of suitable valves placed in the apparatus.

The present invention consists particularly in the vaporization of the oil, without fractionating it, by causing it to pass, with a constant supply, through a series of tubes maintained at a constant temperature. The temperature is maintained sufficiently high to vaporize even the elements of the oil which have the highest boiling points. The most suitable manner of heating for the tubes consists in immersing them in a bath of fused metal.

Another method of vaporization of the oil without fractionation consists in placing the oil directly in contact with the metal in fusion.

The oil can, in this manner, be conducted under the surface of the molten metal.

After having vaporized the oil without fractionation, as described above, the vapor can be brought directly to a burner and can serve for the heating of a generator or other analogous apparatus. In other places, after having vaporized the oil without fractionation, the vapor can be condensed in an appropriate condensing apparatus to serve afterwards as a fuel.

It has been proved that the liquid combustible can be completely distilled without leaving any residue or that it can be used in a carburetor of suitable form to establish an explosive mixture for internal combustion motors.

Various processes for the execution of the invention are described hereinafter and explained by means of annexed drawings which represent diagrammatically various forms of embodiment of apparatus for the treatment of oil.

In Fig. 1, a reservoir of oil A is connected to a reservoir [fol. 973] of compressed air B, which is fed with air compressed by means of the air pump C.

The oil is supplied by the reservoir A by means of a valve A' into a series of narrow tubes D, immersed in a bath of lead in fusion contained in an iron pot E.

As a general rule, the length of the tube immersed in the bath should not be less than about six meters.

The temperature of the bath ought to be at least 700° C, but, because of the absorption of heat by the oil, the temperature of the latter will ordinarily be about 500° C.

The pot E is provided with a cover E′ which is fixed thereon in any suitable manner. It is also provided with a hole E^2 permitting the introduction of metal. The series of tubes D ends in a separating chamber F also immersed in the molten metal contained in the reservoir E. The level of the molten metal ought, preferably, to reach a place in the interior of the orifice E^2, in such a manner as to reduce the surface subjected to oxidation.

The separator F is represented as being connected to three conduits f, f', f^2. The conduit f connects with a worm G through which passes the vapor escaping from the worm D.

The worm G is chilled in any suitable manner and the vapor condensed therein.

The above will be, speaking in a general manner, the method used in *in* a factory to treat oil with a view to producing capable of being vaporized or the improved combustible.

Hereinafter is described an example of treatment of the oil to be vaporized. This oil to be vaporized is an intermediate oil having a density of 0.85 to 0.87 and is extracted from natural petroleum.

This oil is called "gas oil" or "solar oil."

The following data are those that have produced the best results:

Diameter of tube	4.76 mm.
Length of tube	6.096 m.
Temperature of bath	700° C.
Supply of oil per hour	27.216 Kg.
Pressure at which the oil is supplied	45.360 Kg. per 6.45 sq. cum.

It is evident that, if the diameter of the tube is increased or diminished, the heating surface will be increased or diminished in consequence, which will permit a proportionally larger or smaller quantity of oil to be fed per hour. For a [fol. 974] constant supply, the length should be modified

accordingly to be able to maintain the desired relation between the transverse surface and the length of the conduit or tube.

One part of the oil vapor can be brought from the separating chamber F through the regulating valves f^3, f^4 to the burner H placed in a manner to heat the metallic bath contained in the reservoir E.

When it is desired to use the vapor directly, after its formation (for example, if the apparatus is used for the production of combustible on a motor vehicle), the condenser apparatus is done away with. The secondary conduit f^5, which is shown diagrammatically, can be connected with *to* a burner placed under a steam boiler or other arrangement designed to produce heat or energy.

In passing from the worm D into the separating chamber F, the vapor can entrain with it a little quantity of unvaporized — and impurities. The oil and the impurities are led through the pipe f^2 and the cooling worm J into the reservoir K with an overflow K^1.

The superfluous and non vaporized oil as well as the impurities, are led into the reservoir K under a constant head I—I contained in the chamber K'. The oil contained in the reservoir K is then forced by the pump L into the reservoir A.

In applying this process, it is necesary to take care that the pressure in the oil reservoir, the temperature to which the oil is raised, and the speed of its current through the vaporizer be maintained constant. To this end, the circuit is provided with suitable regulating valves which receive, at the beginning of the operation, the desired position which should not be changed during the entire operation.

The temperature of the lead bath ought to be sufficiently high to volatize the element or constituent of the oil having the highest boiling point. The continuity of the operation is of fundamental importance.

In the process which is going to be described, it is important to remember the following:

The oil enters the hot conduit where it is vaporized. The latent heat of vaporization prevents the temperature of the vapor from reaching that of the bath. To this end the quantity of oil which passes through the apparatus is preferably regulated. The vapor continues to absorb heat

but its temperature does not rise to an appreciable extent.

It results from this that the heat is used in producing the [fol. 975] chemical transformation of heavy hydrocarbons into light hydrocarbons. A certain point is reached during the passage of the vapor through the worm, at which each subsequent heating will produce a constant rise in temperature, which indicates that the chemical transformation is finished. It is this point in the apparatus that determines the length of the worm before being immersed in the molten metal, given that the vapor ought not be heated beyond this special point. It is then immediately led into a condenser. If sufficient account is not taken of the foregoing, a conversion of the vapor into permanent gas results.

If the above precautions are meticulously observed, any overheating will not be produced and, due to these means, the oil is vaporized without undergoing fractional distillation.

With the object of insuring the conversion of the hydrocarbons into more volatile hydrocarbons the oil is maintained at an elevated pressure while it passes through the apparatus. This is realized by retaining the pressure at the discharge end, either in sufficiently closing the escape orifice, as shown in Figs. 2, 3 and 4, or by maintaining the column of oil below the escape orifice, as shown in Fig. 1.

Even when the speed of displacement of the oil ought to be at least equal to the speed which which the oil spreads, it is at times to be recommended, in carrying on the process, to employ a greater speed.

Fig. 2 represents another form of embodiment of the apparatus, in which a reservoir of oil M is connected by means of a control valve M′ to a worm N immersed in a bath of molten metal N′. The worm N is connected at its other end, or discharge end, to a pump N^2 which is, in turn connected to a second worm N^3 immersed in a bath of molten metal N^4. The outlet of the worm N^3 is connected by means of a regulating valve N^5 to a condenser worm N^6 immersed in a condenser chamber N^7.

A pump M^2 feeds the reservoir with oil coming from any appropriate source and at the desired pressure. The functioning of the apparatus is as follows:

The oil taken to the reservoir M is brought to the worm N at a pressure approximately equal to that of the atmosphere and it is vaporized during its passage through the worm.

The pump N^2 pumps the vapor of the worm N and compresses it through the worm N^3 to a high pressure. The vapor is changed in passing through the worm N^3, from a heavier hydrocarbon into a lighter hydrocarbon and after [fol. 976] conversion it is condensed in the condensing worm N^6. Manometers, as M^3 and M^4 are mounted in an appropriate manner on the apparatus.

In regulating, in a suitable manner, a control valve N^5, the resulting pressure thus produced can be regulated in such a manner that the necessary pressure may be obtained in the worm N^3.

Another form of embodiment of an apparatus for realizing this invention is represented in Fig. 3. In this construction, an oil reservoir O if fed with oil by a pump O′ connected to the reservoir A, by means of a conduit O^2. The passage of the oil across the conduit O^2 is regulated by the control valve O^3. To the oil reservoir O is connected another pump O^4 which feeds a worm P,—immersed in a molten metal bath P′,—of oil coming from this reservoir O. The emptying end of the worm P is connected, by means of the valve P^2 to a condensing worm P^3, immersed in a condensing reservoif P^4, and connected at its discharge end, to a separating apparatus P^5. The separating apparatus P^5 is connected to a pump P^6, which communicates, in turn, with the oil reservoir O. The oil coming from the reservoir O is vaporized in the worm P and the vapor is then condensed in the condensing worm P^3. The condensed oil runs into the separating apparatus P^5, which permits of the expulsion, through the vent P^8, of all permenent gas which may be formed during the operation. The oil received in the apparatus P^5 can either be forced back by a pump into the reservoir O, to undergo a subsequent treatment, or be discharged through control valve P^7. The necessary pressure can be obtained in the worm P by regulating the pump O^4 in a suitable manner and the regulating valve P^2. Due to this arrangement, the pump O^4 causes to circulate a quantity of oil, much larger, for a unit of time, than the pump O′ diverts into the weir O. In re-running, in this manner, the condensed oil, a much larger yield of lighter hydrocarbons is obtained.

Another form of embodiment of the apparatus is shown in Fig. 4. In this form of embodiment, a pump R feeds oil, taken from a receptacle R′, to a worm R^2, immersed in a molten metal bath R^3.

The outlet orifice S of the worm is located substantially at the bottom of the molten metal bath, and is located beneath a perforated metal plate S′. The receptacle containing the molten metal bath is provided with a hermetic cover T, as shown, and through the top of the said cover passes a [fol. 977] conduit T′ which is connected at its other end to a condensing worm V. The end of conduit T′, placed within the cover T′ is perforated as at T^2 and supports a solid baffle T^3, which equally supports a perforated baffle plate T^4.

A valve W is placed in the conduit T′ and, in suitably regulating the valve, on- can obtain the pressure desired in the space above the molten metal.

In causing this apparatus to function, the oil is placed in circulation through the worm R^2 and it is discharged hot through the venting orifice S under the perforated baffle S′. The oil rises upwardly through the mass of molten metal and is thus vaporized; the vapor passes through the baffle plate T^4 through the perforations T^2 into the conduit T′ and from there to the worm V.

Although various methods of embodiment of this invention have been described above, the invention is not limited to these special methods, but certain details of the invention can be modified, provided that these modifications remain within the spirit of the invention.

Résumé

1. A process of vaporization of oil without fractionation, which consists in:

a) In causing the oil to pass, with a constant supply, through an apparatus in which it is exposed to a constant temperature, sufficiently high to vaporize the constituent having the highest boiling point, the speed of the oil not being less than that at which the same oil will spread if it is placed in contact with the hot vaporizing surface;

b) In heating the oil in a bath of molten metal maintained at a constant temperature;

c) In sending the oil at a constant speed through a series of narrow tubes maintained at a constant high temperature;

d) In that the tubes are immersed in a bath of molten metal;

e) In that the oil is sent, at a constant supply, through a conduit heated only by radiation.

2. A process for the treatment of oil capable of use as fuel, consisting in distilling the oil without fractionation.

3. In an apparatus for vaporizing oil without fractionation, the combination:

a) with a feed reservoir for oil and a compressed air reservoir connected to the said oil reservoir, of a series of [fol. 978] narrow tubes connected to the said reservoir for the feeding of oil and immersed in a bath of molten metal, due to which the oil is sent rapidly through the tubes, with a constant supply and is vaporized;

b) With the narrow tubes, of a separator equally immersed in a bath of molten metal;

c) With the distillation apparatus, of a condenser in which the oil is gathered in the liquid state;

d) With the oil feed reservoir and the distilling apparatus, of an overflow reservoir of suitable type between the separator and the feed reservoir, whereby a constant pressure can be maintained in the separator;—a burner being capable of being connected to the said separator and placed in a manner to heat a bath of molten metal.

H. A. Kittle, by J. Bonnet-Thirion, Attorney.

4226

[fol. 979]

PETITIONER'S EXHIBIT 132

C. W. TURNER.

APPARATUS FOR DISTILLING HYDROCARBON OIL.

APPLICATION FILED JULY 21, 1908.

1,046,683. Patented Dec. 10, 1912.

2 SHEETS—SHEET 1.

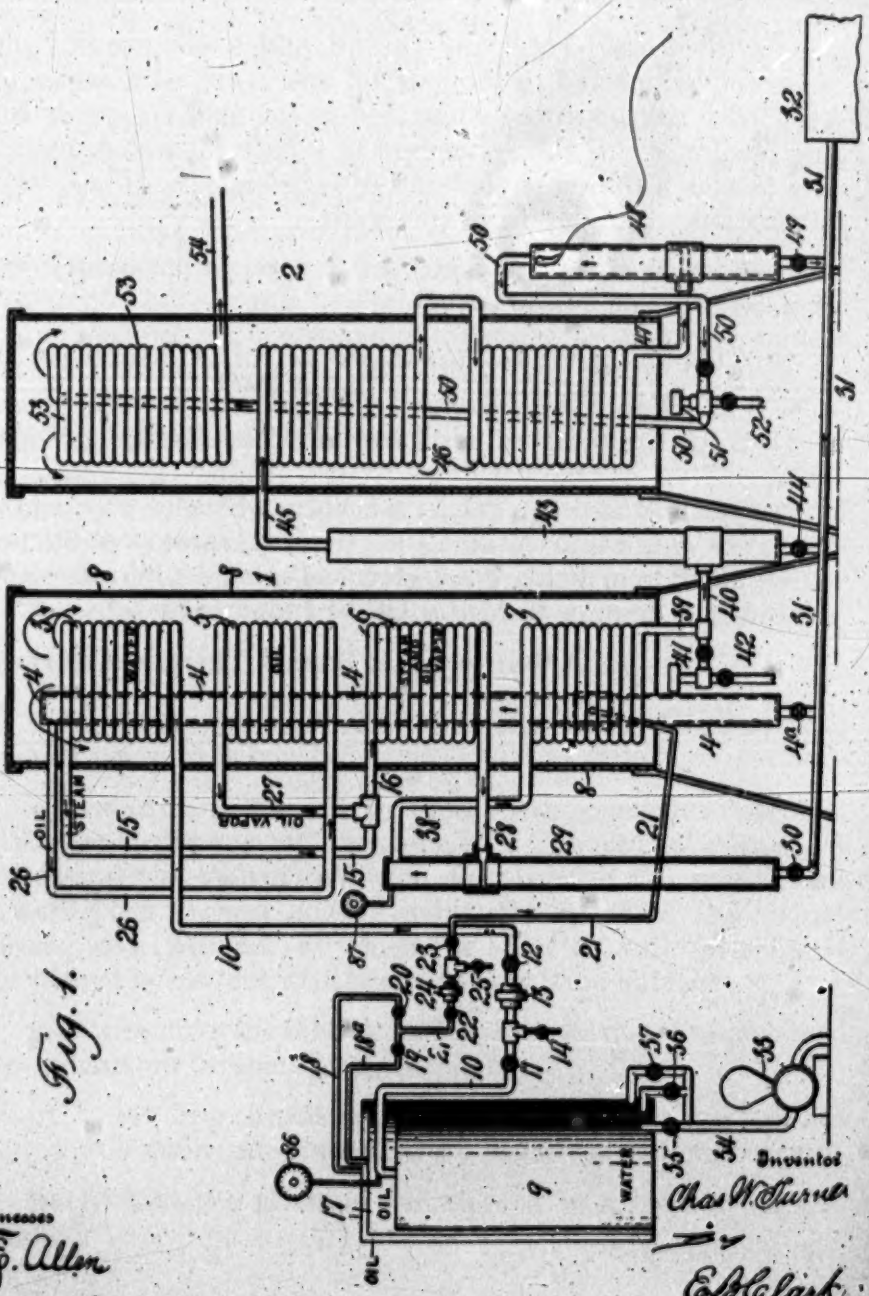


Fig. 1.

PX 132/1

[fol. 980]

C. W. TURNER.

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2 SHEETS—SHEET 2.

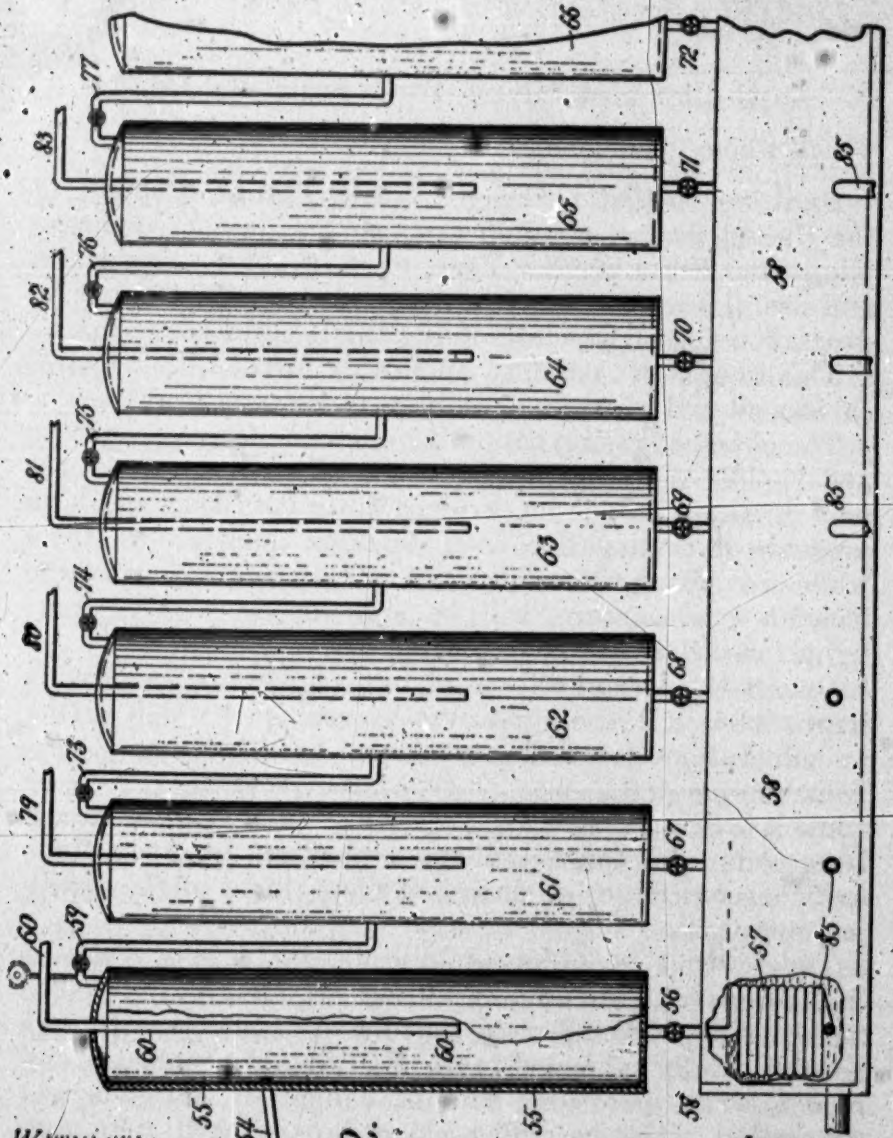

Fig. 2.

WITNESSES.

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Charles Worth Turner, of Brooklyn, New York

Apparatus for Distilling Hydrocarbon Oil

1,046,683. Specification of Letters Patent. Patented Dec. 10, 1912

Application filed July 21, 1908. Serial No. 444,674

To all whom it may concern:

Be it known that I, Charles Worth Turner, a citizen of the United States, residing at Brooklyn, in the county of Kings and State of New York, have invented certain new and useful Improvements in Apparatus for Distilling Hydrocarbon Oil, of which the following is a specification.

This invention relates to apparatus for distilling hydrocarbon oil and obtaining products of various gravities.

The object of my invention is to provide for economically and rapidly distilling hydrocarbon oil, such as petroleum or a distillate therefrom, by subjecting it to heat and high pressure in combination with steam or superheated steam while circulating through heated coils, whereby part of the heavier hydrocarbons will be split or cracked to form lighter distillate liquid products.

One of the special objects of my invention is to provide improvements in the apparatus by means of which earthy or mineral matter and asphaltum, or other heavy carbonaceous material, may be separated from the petroleum while it is being heated and before being fed into the vaporizing coils; also for separating asphaltum, or other dense carbonaceous material, during various stages of the distilling operation.

The present invention embraces certain improvements in the apparatus covered by Patent No. 726,379, granted to me April 28, 1903, whereby petroleum of low gravity may be successfully subjected to the distilling, decomposing and recomposing operations without danger of the coils and connecting pipes becoming clogged or choked with carbonaceous deposits.

The matter constituting my invention will be defined in the claims.

I will now describe my improved apparatus by reference to the accompanying drawing, in which——

Figure 1 represents a side elevation, with parts in section, of the generating or distilling part of the apparatus. Fig. 2 represents an elevation, with parts in section, of the condensing and separating tanks for obtaining various liquid products of different specific gravities.

The distilling or generating part of the apparatus comprises two columns of coils 1 and 2 composed of different sections of coils, suitably disposed separating drums of comparatively large diameter and the necessary connecting pipes for effectively and rapidly carrying out the process of distilling crude petroleum or other hydrocarbon of low gravity. In the column 1 the different sections of coils are superimposed one above another within a heat retaining jacket 8. The steam generating and superheating coil 3 is preferably placed at the top of the casing where the temperature is usually the highest, and the oil vaporizing coil 5 is located immediately below the same so that the steam and oil vapor may be readily brought together in a mixing pipe. Between the outer oil feed tank and the coil 5 I have found it advantageous to interpose an oil heating and separating drum 4 which preferably extends from the base of the column up through all of the coils to near the top of the jacket 1 as shown in Fig. 1. The coils are preferably constructed of pipe having extra thick and strong walls, adapted to stand pressure of several hundred pounds to the square inch. In the apparatus which I have in use the pipe is two inches in diameter, while the heating and separating drum 4 is about five inches in diameter and may be of a larger diameter, up to ten inches or more. This heating and separating drum 4 serves the important purpose of preliminarily heating the crude oil and at the same time permitting the contained mineral matter and asphaltum, or other heavy carbonaceous material, to settle into the lower and cooler end from which, at suitable intervals, such heavy matter is drawn off through valve 4ª and discharged through pipe 31 into a tank 32. Below the oil vaporizing coil 5 is located a coil 6 for mixed steam and oil vapor and at the base of the column is located a combining and superheating coil 7. In this coil 7 the steam and oil vapors are highly superheated and part of the steam is decomposed by the oxygen combining with carbon to form carbon monixid, while hydrogen is liberated. This nascent hydrogen immediately combines with a portion of the hydrocarbon

present to form lighter hydrocarbons. I therefore obtain an increased yield of lighter hydrocarbon oils from crude petroleum.

The supply tanks for water and oil under pressure and the various feed and connecting pipes are constructed and arranged as follows:—The water supply tank 9 and two oil supply tanks 17 are in practice located on a suitable [fol. 982] foundation and are connected at their lower end with a water force-pump 33 having a pipe 34 and branches, provided with valves 35, 36 and 37, connecting with each tank. The water supply being shut off from the oil tanks by closing valves 36 and 37, both of the tanks 17 may be first filled with oil, such as crude petroleum, in any desired manner, and when it is desired to force oil into the vaporizing coil, water will be admitted under pressure into one of the tanks by opening valve 36, thereby forcing oil out through the upper feed pipe 18 to the coil. The water feed pipe 10 connects with the top of tank 9 and with the base of the coil 3. This pipe is provided with the stop valves 11 and 12, an intermediate check-valve 13 and a test cock 14. From the top of coil 3 a steam discharge pipe 15 extends out through the jacket 8 and downward to a mixing pipe 16, with which also connects the oil vapor pipe 27. In order to determine approximately the quantity of water supplied through the pipe 10, valve 12 is closed, the test cock 14 fully opened and the valve 11 partly opened and adjusted so that the desired flow will be discharged through the test cock; this having been ascertained by observation the test cock 14 is closed and valve 12 opened, leaving valve 11 at the proper adjustment for feeding the desired quantity or proportion of water into the coil 3. The check-valve 13 prevents the back flow of water through pipe 10. With the tops of the oil tanks 17 connect the two feed pipes 18 and 18^a which unite with the single feed pipe 21, and said pipes 18 and 18^a are provided, each with a valve 19 and 20. The oil feed pipe 21 connects with the heating and separating drum 4 and is provided with the stop valves 22 and 23, the intermediate check-valve 24 and a test-cock 25. The flow of oil through pipe 21 is regulated by means of a test-cock 25 and adjustment of valve 22 as above described with reference to the test cock and valve on the water pipe 10. With the upper end of the heating and separating drum 4 connects the oil discharge pipe 26 which extends downward and connects

with the base of the oil vaporizing coil 5. An oil-vapor discharge pipe 27, leads from the top of coil 5 and connects through a T-fitting with the mixing pipe 16 which leads into coil 6 for mixed steam and oil vapor. At the base of coil 6 a discharge pipe 28 connects with a separating drum 29 which is provided at its base with a discharge pipe, having a valve 30, opening into the main discharge pipe 31 connecting with the receiving tank 32. Any tarry or other thick carbonaceous matter which may form in coils 6 will be blown into the separating drum 29 and after a sufficient quantity of heavy hydrocarbon accumulates in such drum it may be discharged by opening valve 30. Pipe 38 connects near the top of drum 29 and conducts mixed steam and oil-vapor into the top of the combining and superheating coil 7 from the base of which leads the outlet pipe 39, connecting with pipe 40 which connects with the separating drum 43 and is also provided with a burner 41 which may be provided with a valve. A pipe and valve 42 may connect with the burner for supplying fuel gas when desired. In practice, however, I burn at the burner 41 part of the gaseous mixture which passes from the combining and superheating coil 7. The main volume of vapor or gas will pass from coil 7 into the separating drum 43. The heavier hydrocarbon will be separated in drum 43 and may be discharged therefrom by opening valve 44. A vapor-gas outlet pipe 45 connects with the top of drum 43 and with the top of the combining and decomposing coil 46 in the column 2, where decomposition and recomposition of hydrocarbons are effected. The coil 46 may be composed of two sections having an outside connection as shown and from the base of the lower section a pipe 47 connects with a separating drum 48 having at the bottom an outlet pipe and valve 49 which connects with the drain pipe 31 leading to tank 32. A vapor-gas outlet pipe 50 leads to a burner 51 and thence passes up through the column of coils to the top of an upper section of coils 53 in which the operation of still further decomposing and recomposing hydrocarbons are effected. From the base of this coil extends a vapor-gas outlet pipe 54 leading to the first condenser tank 55. A pipe 52 may conduct fuel gas to the burner 51.

The condenser tank 55 is provided at the bottom with a draw-off pipe and valve 56 leading to a cooling coil 57 located in the water tank 58. To the top of tank 55 a valved

vapor pipe 59 extends downward and connects with the the succeeding condenser tank 61. A separate vapor outlet pipe 60 connects centrally with the top of tank 55 and extends downward below the middle portion thereof for conducting off a different density of vapor from that which passes off through pipe 59. In practice, I provide a series of condenser tanks and have herein shown such tanks 61, 62, 63, 64, 65 and 66 and I may employ sixteen or more of such tanks in series for condensing and separating hydrocarbon distillates of different gravities. These tanks are connected to cooling coils like that shown at 57 in the water tank 58 and each of said coils is provided with a draw-off pipe 85. The tanks are connected in series with pipes and valves 73, 74, 75, 76 and 77 and each tank has a separate vapor discharge pipe, 79, 80, 81, 82, 83, etc.

I preferably connect with the water and oil tanks 9 and 17, Fig. 1 a pressure gage 86 and maintain in said tanks a [fol. 983] pressure of about 100 pounds to the square inch. There is also connected to the separating drum 29 a pressure gage 87 which will indicate the vapor pressure in the coils 6 and 7. This pressure is preferably about sixty pounds to the square inch. It will be readily understood that with these high pressures and with a sufficiently high temperature which may be from 400 to 800 degrees Fahrenheit, in the coils 6 and 7, the circulation of water, oil and combined vapors will be very rapid and that distillation will be effected with corresponding rapidity. In the column 2 I preferably carry the temperature up to a degree between 1000 and 1200 or 1400 degrees F.

The apparatus having been constructed and connected substantially as above described and shown in the drawings and the tanks 9 and 17, respectively, filled with water and petroleum the operation of distilling and separating the oil into products of different gravities may be conducted as follows: The columns of coils may be primarily heated by supplying fuel gas to the burners or burning any waste material saturated with oil at the base of the columns. A sufficient heat having been raised in the heat retaining jackets, the pump 33 will be started, thereby forcing water into the base of tank 9 and one of the tanks 17, now by properly adjusting the valves in the supply pipes as previously described, water will be supplied under pressure to the steam generating coil 3 and oil will be sup-

plied under pressure to the preheating and separating drum 4 and thence by pipe 26 to the oil vaporizing coil 5. As soon as a sufficiently high degree of heat has been attained, superheated steam will pass by pipe 15 to the mixing pipe 16 and at the same time oil vapor will be passed by pipe 27 to said mixing pipe 16 and the mixture will be forced through coil 6 where the steam and oil vapor will be more intimately mixed and heated and then discharged through pipe 28 into the separating drum 29. Here the heavier hydrocarbons, tarry matter and earthy material or other impurities will be arrested and settle to the bottom, while the lighter vapors will be conducted by pipe 38 into the combining and superheating coil 7 in which will be produced vapor-gas. This gas bein combustible, will be admitted to the burner 41 where it is ignited. The flame and hot products pass up through the column of coils and thence down between the coils and the heat retaining jacket 8, from the lower end of which the spent products escape. Combustion of the vapor-gas being perfect within the heating jacket, no smoke or sooty matter passes out from the base of the heat retaining jacket. The heavy hydrocarbons containing paraffin, tarry matters and other impurities which may settle in the drum 4 and in drum 29 will be, at suitable intervals, drawn off, respectively through the valves 4ª and 30 and conducted to the receiving tank 32. The vapor-gas discharged from coil 7 through pipes 39 and 40 into the separating drum 43 will also part with the tarry matter and other heavy impurities which will settle in said drum, and may be drawn off through pipe and valve 44 and conducted to the tank 32. The vapor-gas passing off from drum 43 will be conducted through the coils 46 and 53 where they are subjected to a high heat, usually about 1000 degrees Fahrenheit, thereby causing the heavier hydrocarbons to be split up or cracked into hydrocarbons of a higher specific gravity. The high heat in these coils may cause naphthalene to be formed and such product will be, to a great extent, separated in the drum 48. Paraffin and tarry matter may be also separated in the drum 48. By successively causing separation of heavy carbonaceous matter, including paraffin and naphthalene, a superior quality of lubricating oil will be collected in the first two or three condensation tanks of the series 55

to 66. In the succeeding tanks 63, 64 and 65, a high grade of illuminating oil or kerosene will be deposited. In the succeeding tanks of the series, which may be of any desired number, there will be separated various gravities of lighter oils and any desired number of these light oils such as benzine, gasolene, etc., may be separately drawn off and stored.

The process herein described is made the subject of my co-pending application, Serial Number 727,925.

Having described my invention, what I claim as new and desire to secure by Letters Patent, is—

1. In apparatus for distilling hydrocarbon oil, the combination with an oil vaporizing coil, of an upright heating and separating drum having at the lower end a discharge pipe and valve for drawing off heavy matter, an oil feed pipe connecting with the drum near its lower end, means for forcing oil under pressure through said feed pipe, an outlet pipe connecting with the top of the drum and with said vaporizing coil, and a vapor discharge pipe leading from the coil, substantially as described.

2. In apparatus for distilling hydrocarbon oil, the combination with an oil vaporizing coil, a steam generating coil, and a mixing coil for steam and oil vapor, of means for supplying oil and water, respectively to the oil vaporizing and steam generating coils, outlet pipes connecting said vaporizing and steam generating coils with the mixing coil, an upright separating drum having a discharge pipe and valve at its lower end, and a pipe connecting the mixing coil with said drum, substantially as described.

[fol. 984] 3. In apparatus for distilling hydrocarbon oil, the combination with an oil vaporizing coil, of an upright heating and separating drum having at the lower end a discharge pipe and valve for drawing off heavy matter, an oil feed pipe connecting with the drum, a steam generating coil having a water feed pipe, means for forcing oil and water through said feed pipes, a mixing coil for steam and oil vapor, pipes connecting said vaporizing coil and the steam generating coil with said mixing coil, a second separating drum having a discharge pipe and valve at its lower end, and a pipe connecting the mixing coil with the second separating drum.

4. In apparatus for distilling hydrocarbon oil, the combination with a set of coils for combining and superheating vapor-gas and a separate coil for further heating said vapor-gas and promoting the distilling operation, of an intermediate separating drum in which heavy tarry matter is deposited, whereby the distilling operation may be made continuous, and means for heating the coils, substantially as described.

5. In apparatus for distilling hydrocarbon oil, the combination with a decomposing and recomposing coil and means for supplying it with mixed oil and water vapor-gas, of an outer separating drum having means for drawing off deposits of heavy carbonaceous material, a condensation tank and a pipe connection from said drum to said tank, substantially as described.

6. In apparatus for distilling hypdrocarbon oil, the combination with separate vaporizing coils for oil and water and combining and superheating coils, of separating drums, a series of condensation tanks connected by vapor pipes, a cooling coil in a water tank connected with the lower end of each tank of the series, substantially as described.

7. In apparatus for distilling hydrocarbon oil, the combination with combining and superheating coils and separate coils for further combining and highly heating hydrocarbon vapors, of an interposed separating drum of larger diameter than the coils, a draw-off pipe for heavy products at the lower end of said drum, a discharge pipe at the top leading into the second set of coils, and an intermediate inlet pipe leading from the first set of coils, substantially as described.

In testimony whereof I affix my signature in presence of two witnesses.

Charles Worth Turner.

Witnesses: John A. Schilling, William Williams.

[fol. 985] PETITIONER'S EXHIBIT 133

No. 1308. (Coat of Arms.) A. D. 1891

Date of Application: 24th Jan., 1891. Accepted: 14th Mar., 1891

Complete Specification

Improvements in the Continuous Distillation of Hydrocarbon and other Oils and Liquids

I, Carl Maria Pielsticker, of 43, Connaught Road, Harlesden, N. W., in the County of Middlesex, Engineer, do hereby declare the mature of this invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

My invention relates to improvements in the distillation of hydrocarbon and other oils and liquids by means of which the operation of distillation is conducted in a continuous manner.

In the Specification to Letters Patent granted to me in Great Britain under No. 1706 and dated April 10th 1882 I described a method in which the hydrocarbon oil was forced under pressure by means of a force pump, or a steam injector into a coil open at the other end, in which coil the oil was heated to its distilling point, the heated oil entering from the coil into a heated retort in which it was vaporised and again condensed in a cooler connected with the retort.

In employing this apparatus it was found difficult to so regulate the temperature of the coil, that all the oil at once assumed vapour form on entering the retort, while at other times the coil became so superheated that a portion of the oil became converted into permanent gas.

Moreover the coil being directly exposed to the action of a high temperature was burned through in a short time and finally it was found impossible to clean the coil from the carbon deposited therein from the oil passing through it. These defects have been obviated by improvements set forth in my Specification No. 6466 of 1890 and the object of the improved apparatus which I will now proceed to describe by reference to the accompanying drawing is to obtain a yet more perfect and continuous operation.

On the accompanying drawings:

[fol. 986] Figure 1 is an elevation showing general arrangement of oil tank, pump, and heating coil.

Figure 2 an elevation showing the arrangement of retort and condenser.

Figure 3 is an enlarged section through the dome and goose neck.

Figure 4 is a longitudinal section through the retort showing arrangement of baffle plates.

Figure 5 is a transverse section through the same.

Figure 6 illustrates the methods of connecting the pipes by means of short bends.

Figure 7 is a detail of a tar outlet from retort fitted with steam ejector.

Figure 8 a sectional elevation of a column still, and

Figure 9 is an elevation showing the arrangement of a retort and second heating coil.

A the oil tank.

B steam coil.

C pump or injector.

D. heating coil.

E block of iron.

F iron cover.

G inlet to retort, G^1 outlet valve to second retort D^1.

H steam connection to heating coil, H^1 steam injector to second coil D^1.

I retort, K baffle plates.

L passage at bottom of plate.

M movable cover of retort.

N tart outlet valve on retort I.

O steam inlet to valve N.

P the dome, P^1 oil pipe.

Q goose neck, Q^1 second bend, R contraction or valve in goose neck.

S baffle plates in dome.

T cup inside dome.

U small vessel or condenser.

U^1 second vessel or condenser.

V draw off cocks.

W column still.

X baffle plates in column still.

Y draw off cock for tar.

Z steam ejector.

The oil to be distilled is contained in a tank A, in which it [fol. 987] is heated by means of a steam coil B, or otherwise. From this tank the oil is forced by means of a pump C, or otherwise, into a coil D which is formed of a number of iron pipes, embedded or inserted into a solid block of iron or refractory material E closed by covers F as described and claimed in my Specification No. 6466 of 1890.

Between the force pump C and the inlet of the coil D, a steam connection H is provided for the purpose of emptying the oil contained in the coil D at the end of the operation by a steam blast into a retort I into which the other end of the coil D leads; otherwise when the pumping is stopped the oil remaining in the coil D would speedily become carbonised and choke the coil.

Between the pump C and the coil D and between the coil D and retort I expansion joints may be provided. The retort I is provided with a number of baffle plates K causing the oil vapours to take a lengthened passage through the retort, before they can enter the condenser U.

A passage L is left in the lower part of the baffle plates in order to obtain the flow of the tar or residuum to the draw off cock.

The end of the retort opposite to the inlet of the oil is closed by a removable cover M.

Nearly at the lower end of the cover is fitted a valve N, for the removal of the tar or residue during the operation of distilling, a steam inlet O being connected with the tar outlet, in order to blow steam when the tar outlet is opened, which not only assists in the removal of the thick tar or the residue but more particularly prevents air from entering the retort, which air would form a dangerously explosive mixture with the highly heated oil gases inside the retort.

It will be evident that since a constant supply of oil is thus fed into the retort I and the residuum of this oil or other liquid entering the latter, by preference from the highest point of the coil, being constantly removed during the distillation, this distillation thus becomes continuous.

A dome P and goose neck Q connects the retort with a condenser. The dome P may be enlarged at its base forming a sphere, and may be provided at its lower end inside with a cup shaped projection T, into which any oil collects which may condense in the dome P and from which it may be returned into the retort I or into the supply tank A,

through the pipe P^1. This dome may be provided with a number of baffle plates S, which force the vapours to come [fol. 988] in contact with the inner surface of the dome P, where the heavier portion of them are caused to condense and returning to the more heated surface of the retort, are reduced in gravity and finally distill over and condense in the condenser.

The condenser may either be an ordinary coil or a surface condenser, the first bend of which reaches into a vessel U nearly to the bottom of the latter, in which part of the vapours condense; the uncondensed portion being led by the second bend Q^1 from the top of the first vessel U to the bottom of the second vessel U^1 and so on through a series of condensing vessels, which are all provided with draw off cocks V, in which the vapours are successively condensed into oil of a number of graduated specific gravities, heavier at the beginning of the series and lighter towards the end of the series.

Or instead of this arrangement, the products of distillation as they pass over from the retort I may be fractionally separated into a number of oils of graduated specific gravities by connecting the heating coil with a column still W, which may be similar to that used in the distillation of benzol, the body of which column still I also divide by baffle plates X and a draw off cock Y for the tar or residue with steam ejector Z.

When it is intended to produce still lighter gravity oils, a valve R may be placed between the outlet of the retort I and the condenser U which may be kept open only so far as to create a certain pressure of the gases inside the retort, or such pressure may be created by means of a steam blast, introduced into the goose neck Q, and blowing in the opposite direction to the flow of vapours which distill over from the retort, or the goose neck Q may be contracted at some point to a much smaller diameter by valve R or otherwise.

In case the crude oil contains a considerable quantity of water, the latter may be separated from the oil by placing the baffle plates horizontally into the retort, over which the oil and water flows, presenting in this manner a very extended surface, which is most conducive to rapid evaporation. The coil D and the retort I are kept at the temperature at which only the water distills off, while the oil pumped through the coil and retort is drawn off at the tar

cock Y free from water and in a subsequent operation may be subjected to distillation.

If the manufacture of permanent gas or of very light oil is intended, the retort I is directly connected with a second coil D^1 similar to the first one D; steam, which may pre- [fol. 989] viously have been superheated, being in preference simultaneously admitted with the oil vapours into the second coil D^1 by means of a steam injector H^1 provided for the purpose; the second coil may be kept under pressure by means of a valve G^1 or otherwise, and may be connected with expansion chamber or gasholder and condenser of well known construction.

My apparatus may also be used for the distillation of other liquids besides hydrocarbons, for instance for fats and oils in the separation of fatty acids and glycerine.

Also for the continuous production of distilled water from sea water or the concentration of brine and alkaline solutions, the concentration of sugar solutions, the salt water, alkaline, or other solution being in this case pumped through the heating coil, the greater portion of the water distills over in the retort provided with horizontal baffle plates and which in this case may be provided with an exhauster or vacuum pump. The concentrated salt alkaline or other solution may be drawn off at the draw off cock at the end of the retort.

Having now particularly described and ascertained the nature of my said invention, and in what manner the same is to be performed, I declare that what I claim is:

1. An apparatus for the continuous distillation of hydrocarbon and other oils and liquids consisting of a supply tank, means of heating the same, of forcing the liquid into and through a heated coil connected with a steam jet or blast, from thence into and through a retort provided with baffle plates, and draw off cock fitted with steam ejector, to a condenser; the whole constructed, combined and arranged to operate substantially as hereinbefore described and illustrated on the drawing.

2. An apparatus for continuous distillation of hydrocarbon and other oils and liquids consisting of a supply tank, means of heating the same, of forcing the liquid into and through a heated coil, connected with a steam jet or blast, from whence it passes into and through a retort provided

with baffle plates and draw off cock fitted with steam ejector, thence into and through a second heating coil which may or may not be provided with a steam inlet and the outlet of which may or may not be provided with means of retarding the outflow and which may lead into an expansion chamber and thence to a condenser in communication with a gasholder or other receptacle, the whole substantially as hereinbefore described.

[fol. 990] 3. In apparatus for the continuous distillation of hydrocarbon and other oils and liquids constructed as hereinbefore described and claimed, increasing the velocity of the flow of the liquid through the heating coil from the inlet towards the outlet by a contraction of the outlet as compared with the inlet substantially as and for the purpose specified.

4. In apparatus for the continuous distillation of hydrocarbon oils and other liquids, the application of a steam ejector to the draw off cock for the residue substantially as hereinbefore described.

5. In apparatus for the continuous distillation of hydrocarbon and other oils and liquids, means of forcing the oil out of the coil at the end of an operation whereby the carbonisation of the oil contained in the coil is prevented substantially as hereinbefore described.

6. In apparatus for the continuous distillation of hydrocarbon and other oils and liquids, a dome, connecting a retort with the goose neck and condenser, provided inside at its base with an annular cup, in which the heavier portions of the oil vapours condensed in the dome collect, and from where they can be returned into the supply tank, or into the heating coil, or into the retort, substantially as described.

7. In apparaus for the continuous distillation of hydrocarbon and other oils and liquids constructed as hereinbefore described and claimed, means of separating the distillate fractionally, substantially as described.

Dated this twenty-fourth day of January 1891.

For the Applicant, W. E. Gedge, Agent.

London: Printed for Her Majesty's Stationery Office, by Darling & Son, Ltd.—1891.

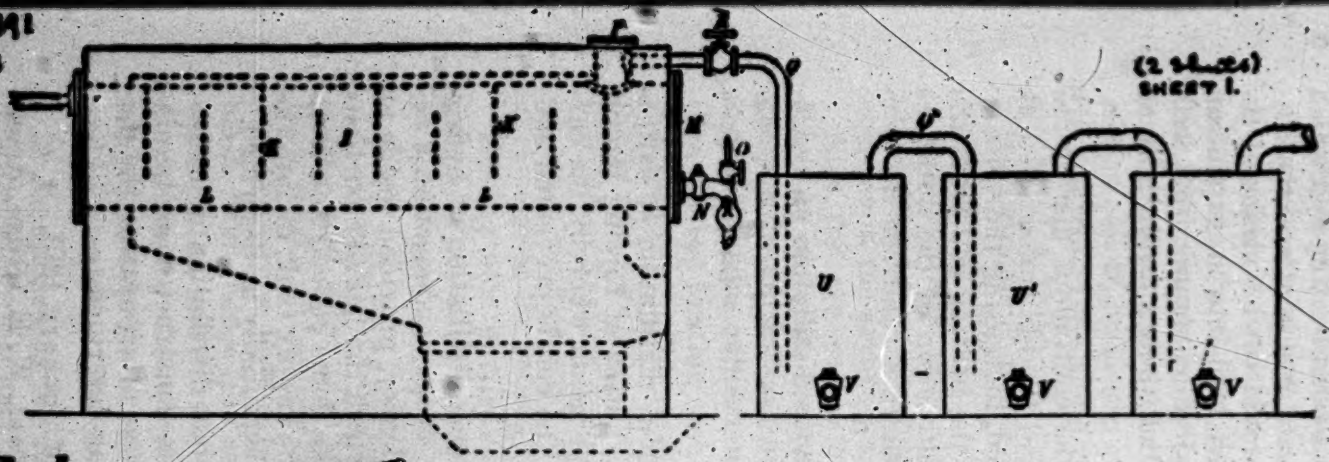
266—378

JAN. 24, 1891
No. 1308

(2 Sheets-Sheet 1.)
SHEET 1.

4242

[fol. 991]



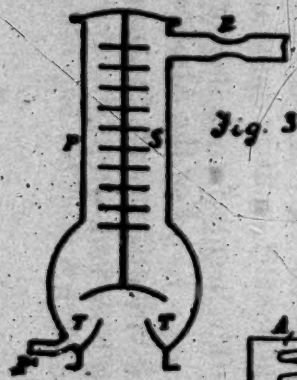
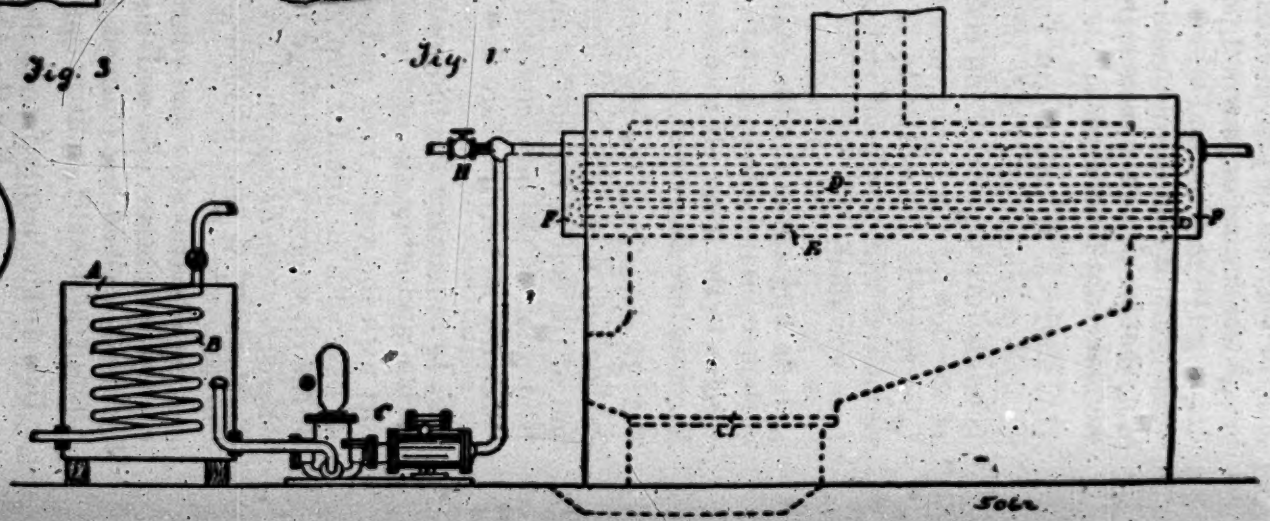
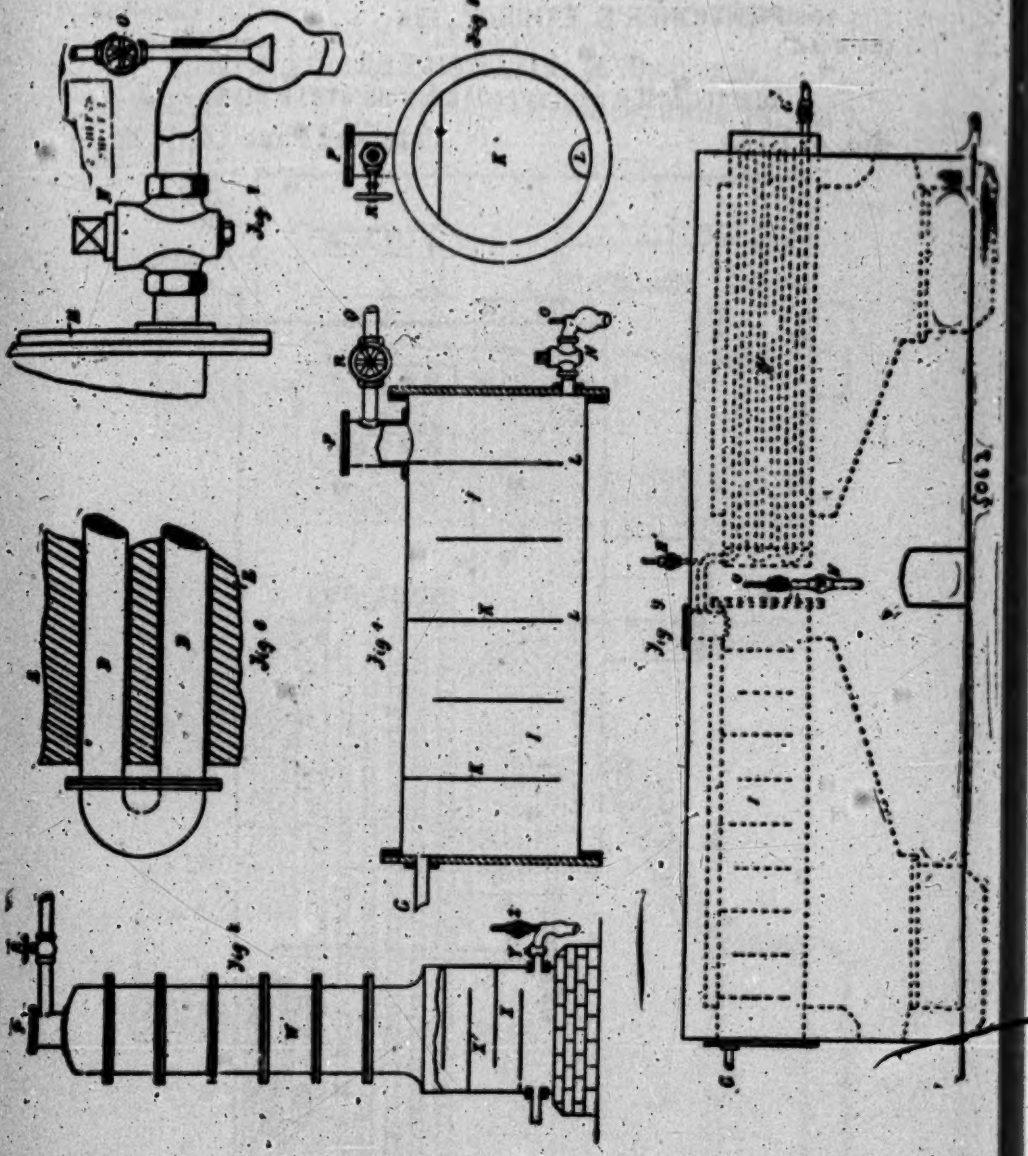


Fig. 3

Fig. 1



[fol. 992]



PETITIONER'S EXHIBIT 134

(No Model.) 5 Sheets—Sheet 1

C. M. PIELSTICKER.

DISTILLATION OF HYDROCARBON OR OTHER OILS.

No. 477,153. Patented June 14, 1892.

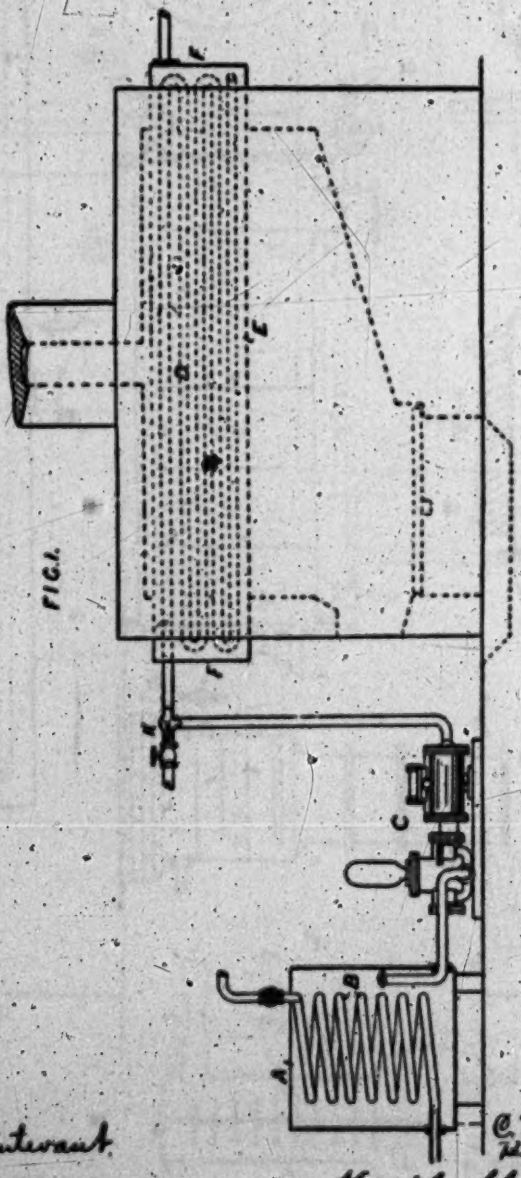


FIG. 1.

Witnesses
Chas. A. Stuntevant
Stephen Jarman

C. M. Pielsticker
by Atty.
Frank Bond Jarman

PA 134-1

4245

[fol. 994]

(No Model.) 5 Sheets—Sheet 2

C. M. PIELSTICKER.

DISTILLATION OF HYDROCARBON OR OTHER OILS.

No. 477,153. Patented June 14, 1892.

FIG. 3.

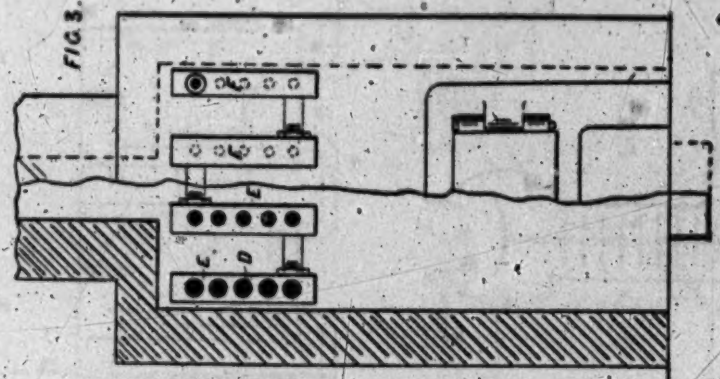
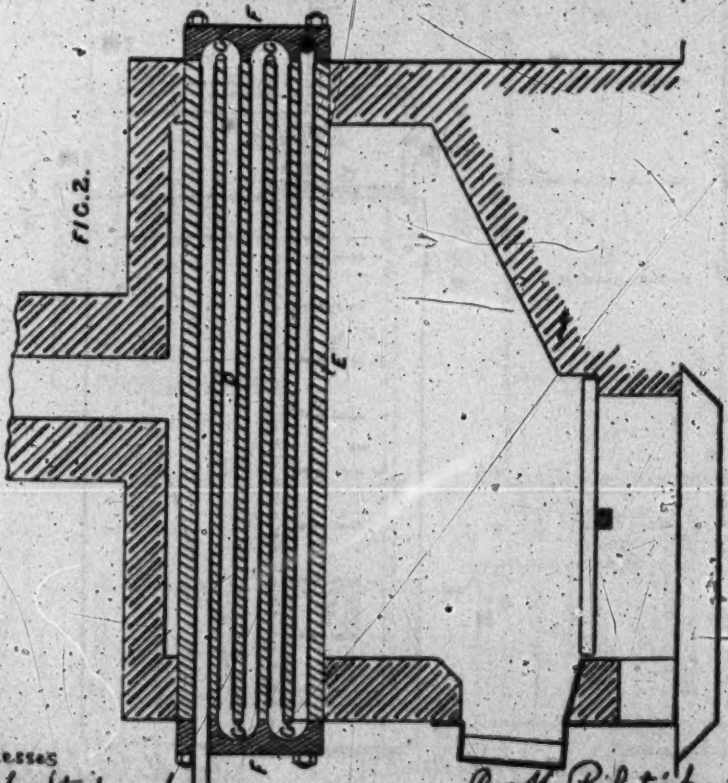


FIG. 2.



Witnesses
Chas. G. Stuntebeck
Stephen Fanning

C. M. Pielsticker
By Atty Thos. Lee Fanning

PX134-2

4246

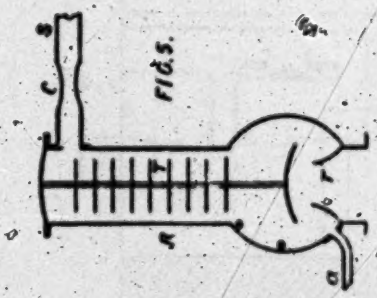
[fol. 995]

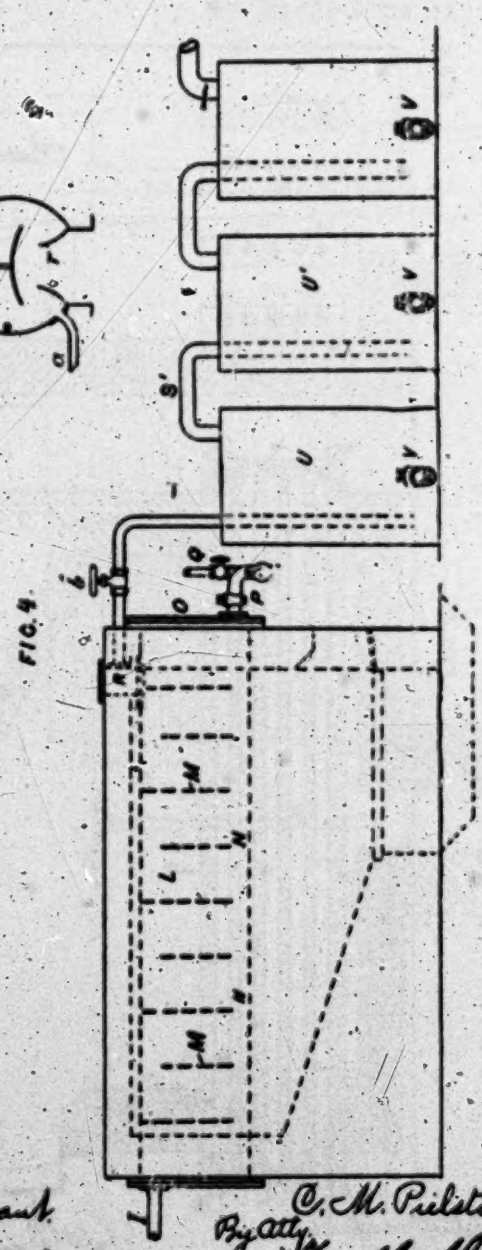
(No Model.) 5 Sheets—Sheet 3

C. M. PIELSTICKER.

DISTILLATION OF HYDROCARBON OR OTHER OILS.

No. 477,163. Patented June 14, 1892.





Witnesses:
Chas. L. Stuntevant.
Stephen Farnsworth

C. M. Pielsticker
By Atty
Thornton & Farnsworth

PE 174-3

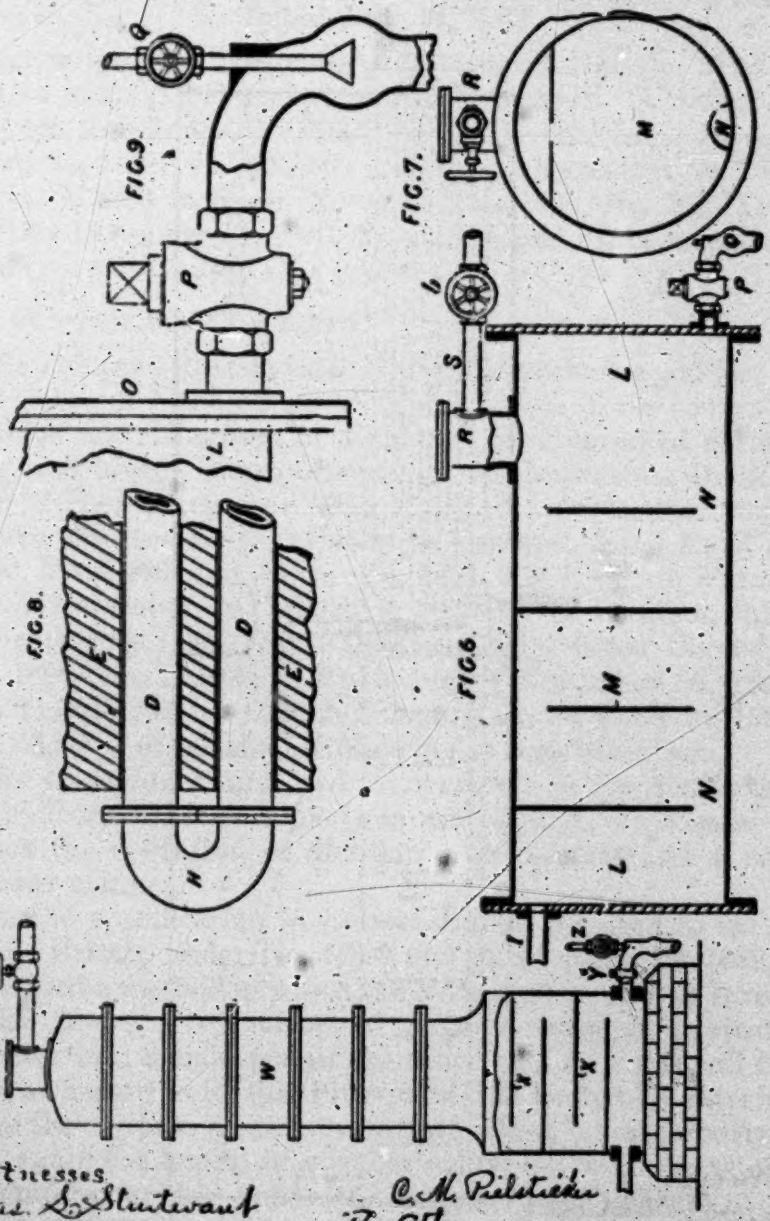
[fol. 996]

(No Model.) 5 Sheets—Sheet 4.

C. M. PIELSTICKER.

DISTILLATION OF HYDROCARBON OR OTHER OILS.

No. 477,153. Patented June 14, 1892.



Witnesses.
Chas. L. Stuntevant
Stephen Jamney

C. M. Pielsticker
By Atty
Frankland Jamney

PA 134-2

4248

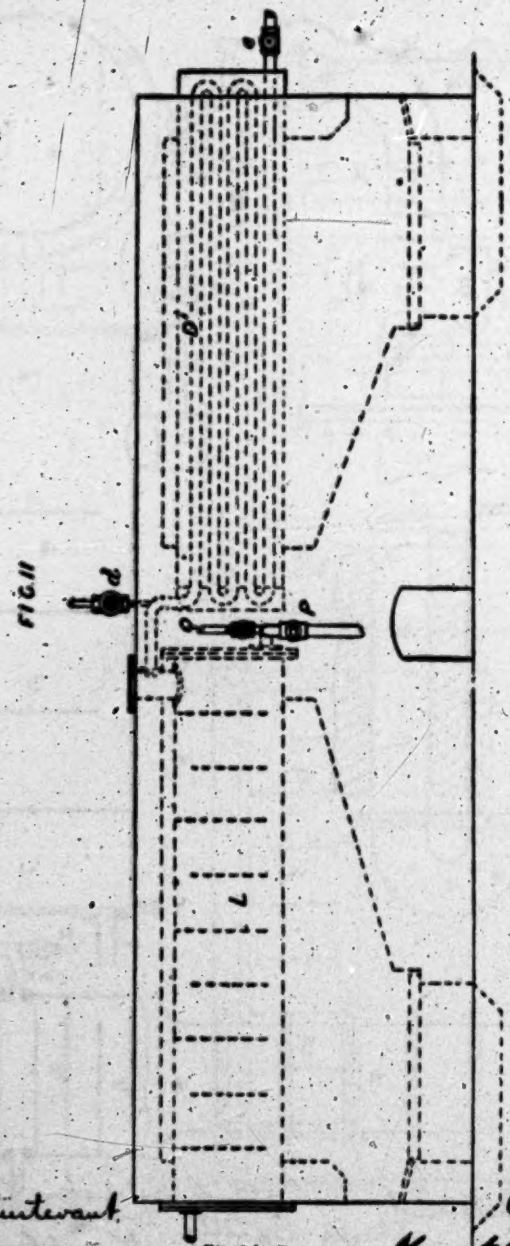
[fol. 997]

(No Model.) 5 Sheets—Sheet 5.

C. M. PIELSTICKER.

DISTILLATION OF HYDROCARBON OR OTHER OILS.

No. 477,153. Patented June 14, 1892.



Witnesses
Chas. L. Stutevant
Stratton Fanning

C. M. Pielsticker.
By Atty
Frank Lord Jones

[fol. 998] United States Patent Office

Carl Maria Pielsticker, of London, England

Distillation of Hydorcarbon or Other Oils

Specification Forming Part of Letters Patent No. 477,153, Dated June 14, 1892

Application filed November 26, 1890. Serial No. 372,721. (No model.) Patented in England April 28, 1890, No. 6,466, and January 4, 1891, No. 1,308; in France November 26, 1890, No. 209,809; in Belgium November 26, 1890, No. 92,883; in Spain November 26, 1890, No. 11,511; in Italy December 31, 1890, No. 28,644, and in Austria-Hungary June 16, 1891, No. 53,380

To all whom it may concern:

Be it known that I, Carl Maria Pielsticker, a subject of the Queen of England, residing at London, in the county of London and Kingdom of England, have invented certain new and useful Improvements in the Continuous Distillation of Hydrocarbon or other Oils and Liquids, (for which I have obtained Letters Patent in England, dated April 28, 1890, No. 6,466, and January 4, 1891, No. 1,308; in France, dated November 26, 1890, No. 209,809; in Belgium dated November 26, 1890, No. 92,883; in Italy, dated December 31, 1890, No. 28,644; in Spain, dated November 26, 1890, No. 11,511, and in Austria-Hungary, dated June 16, 1891, No. 53,380,) of which the following is a specification.

My invention relates to improvements in the distillation of hydrocarbons or other oils and liquids, by means of which the operation of distillation is conducted in a continuous manner.

In the specification to Letters Patent granted to me in Great Britain under No. 1,706 and dated April 10, 1882, I described a method in which the hydrocarbon oil was forced under pressure by means of a force-pump or a steam-injector into a coil open at the other end, in which coil the oil was heated to its distilling-point, the heated oil entering from the coil into a heated retort, in which it was vaporized and again condensed in a cooler connected with the retort. In employing this apparatus it was found difficult to so regulate the temperature of the coil that all the oil at once assumed vapor form on entering the retort, while at other times the coil became so superheated that a portion of the

oil became converted into permanent gas. Moreover, the coil, being directly exposed to the action of a high temperature, was burned through in a short time, and finally it was found impossible to clean the coil from the carbon deposited therein from the oil passing through it.

In the improved apparatus, which I will now proceed to describe by reference to the accompanying drawings, the above-mentioned defects have been obviated and a more perfect operation attained.

On the accompanying drawings, Figure 1 is an elevation showing general arrangement of oil tank or pump and heating coil; Fig. 2, an elevation showing the arrangement of a retort and condenser. Fig. 3 is an enlarged section through the dome and goose-neck; Fig. 4, a longitudinal section through heating-coil; Fig. 5, an end sectional elevation of the same. Fig. 6 is a longitudinal section through the retort, showing arrangement of baffle-plates. Fig. 7 is a transverse section through the same. Fig. 8 illustrates the methods of connecting the pipes by means of short bends. Fig. 9 is a detail of the tar-outlet from retort fitted with steam-ejector; Fig. 10, a sectional elevation of a column-still; and Fig. 11 is an elevation showing the arrangement of a retort and second heating-coil.

A is the oil-tank, *a*, oil-pipe; B, steam-coil; *b*, valve or outlet of retort; C, pump or injector; *c*, contraction or valve in goose-neck; D, heating-coil; *d*, steam-injector to second coil; D′, second heating-coil; E, block of iron; *e*, valve on second coil; F, iron cover; G, channels; H, bends; I, inlet to retort; K, steam connection; L, retort; M, baffle-plates; O, movable cover of retort; N, passage at bottom of plate; P, outlet-valve on retort L; Q, steam-inlet to valve; R, the dome; *r*, cup inside dome; S, goose-neck; S′, second bend; T, baffle-plates in dome; U, small vessel or condenser; U′, second vessel or condenser; V, draw-off cocks; W, column-still; X, baffle-plates in column-still; Y, draw-off cock for tar; Z steam-injector.

The oil to be distilled is contained in a tank A, in which it is heated by means of a steam-coil B or otherwise. From this tank the oil is forced by means of a pump C or otherwise into a coil D, which is formed of a number of iron pipes—say ten feet long and, say, an inch and a half (more or less) in diameter—the ends of which are open and the whole of the pipes embedded or inserted into a solid block

of iron or refractory material E, provided with longitudinal channels through their entire length, into which the pipes fit. The ends of the pipes are closed by means of an iron cover F, which is provided with channels to G, so that the pipes D form one continuous coil. In this case the cover F can be easily removed and the pipes be occasionally [fol. 999] cleared of the carbon deposited inside from the heated oil by simply forcing an iron rod through the length of each pipe forming the coil. I may connect the open ends of the pipes D by short bends H, which are also removable for cleaning in a similar manner. This construction of the heating-coil is a matter of great importance, since it is impossible to clear an ordinary coil of the requisite length from any carbon adhering inside. Moreover, the coil being loosely inserted into the block of iron or of refractory material E, the whole length of the coil is permitted free expansion, and the joints are in consequence kept tight.

I have found that by passing the oil through the coil with great velocity I in a great measure prevent the deposition of carbon or heavy matter which would soon choke up the coil. I now find it preferable to attain this object by graduating the diameter of the pipes D, forming the coil. For instance, if the entire length of the coil is two hundred feet I construct the first fifty feet of two-inch pipes, the second fifty feet of one-and-a-half-inch pipes, and the last hundred feet of one-inch pipes. I may, however, decrease the diameter of the coil only toward or at the inlet I into the retort.

Between the force-pump C and the inlet of the coil D a steam connection K is provided for the purpose of emptying the oil contained in the coil D at the end of the operation by a steam-blast into a retort L, into which the other end of the coil D leads; otherwise when the pumping is stopped the oil remaining in the coil D would speedily become carbonized and choke the coil.

Between the pump C and the coil D and between the coil D and retort L expansion-joints may be provided. The retort L is provided with a number of baffle-plates M, causing the oil-vapors to take a lengthened passage through the retort before they can enter the condenser. A passage N is left in the lower part of the baffle-plates in order to allow the flow of the tar or residuum to the draw-off cock.

The end of the retort opposite to the inlet of the oil is closed by a removable cover O. Nearly at the lower end of

the cover is fitted a valve P for the removal of the tar or residue during the operation of distilling, a steam-inlet Q being connected with the tar-outlet in order to blow steam when the tar-outlet is opened, which not only assists in the removal of the thick tar or the residue, but more particularly prevents air from entering the retort, which air would form a dangerously-explosive mixture with the highly-heated oil-gases inside the retort. It will be evident that since a constant supply of oil is fed into the retort L and the residuum of this oil or other liquid entering the latter by preference from the highest point of the coil, being constantly removed during the distillation, this distillation thus becomes continuous.

A dome R and goose-neck S connect the retort with a condenser. The dome R may be enlarged at its base, forming a sphere, and may be provided at its lower end inside with a cup-shaped projection *r*, into which any oil collects which may condense in the dome R and from which it may be returned into the retort L or into the supply-tank A through the pipe *a*. This dome may be provided with a number of baffle-plates T, which force the vapors to come in contact with the inner surface of the dome R, where the heavier portion of them are caused to condense, and, returning to the more heated surface of the retort, are reduced in gravity and finally distill over and condense in the condenser.

The condenser may either be an ordinary coil or a surface condenser, the first bend of which reaches into a vessel U, nearly to the bottom of the latter, in which part of the vapors condenses, the uncondensed portion being led by the second bend S′ from the top of the first vessel U to the bottom of the second vessel U′, and so on through a series of condensing-vessels, which are all provided with draw-off cocks V, in which the vapors are successively condensed into oil of a number of graduated specific gravities heavier at the beginning of the series and lighter toward the end of the series; or, instead of this arrangement the products of distillation as they pass over from the retort L may be fractionally separated into a number of oils of graduated specific gravities by connecting the heating-coil with a column-still W, which may be similar to that used in the distillation of benzole, the body of which column-still I also

divide by baffle-plates X, and a draw-off cock V for the tar or residue with steam-ejector Z. When it is intended to produce still lighter gravity oils, a valve *b* may be placed between the outlet of the retort L and the condenser U, which may be kept open only so far as to create a certain pressure of the gases inside the retort, or such pressure may be created by means of a steam-blast introduced into the goose-neck S and blowing in the opposite direction to the flow of vapors which distil over from the retort, or the goose-neck S may be contracted at some point *c* to a much smaller diameter.

In case the crude oil contains a considerable quantity of water, the latter may be separated from the oil by placing the baffle-plates horizontally into the retort, over which the oil and water flows, presenting in this manner a very extended surface, which is most conducive to rapid evaporation. The coil D and the retort L are kept at the temperature at which only the water distils off, while the oil pumped through the coil and retort is drawn off at the tar-cock Y free from water and in a subsequent operation may be subjected to distillation.

If the manufacture of permanent gas or of very light oil is intended, the retort L is directly connected with a second coil D′, similar to the first one D, steam which may [fol. 1000] previously have been superheated being in preference simultaneously admitted with the oil-vapors into the second coil D′ by means of a steam-injector *d*, provided for the purpose. The second coil may be kept under pressure by means of a valve *e* or otherwise and may be connected with an expansion-chamber or gas holder and condenser of well-known construction.

My apparatus may also be used for the distillation of other liquids besides hydrocarbons—for instance, for fats and oils in the separation of fatty acids and glycerine; also, for the continuous production of distilled water from sea-water or the concentration of brine and alkaline solutions and the concentration of sugar solutions. The concentrated salt, alkaline, or other solution may be drawn off at the draw-off cock at the end of the retort.

Having fully described my invention, what I claim, and desire to secure by Letters Patent, is—

1. In an apparatus for the continuous distillation of oil, a supply-tank, a coil, connections between the two, means for heating both tank and coil, means for forcing the liquid from the supply-tank through the said coil, a steam jet or blast in connection with said coil, a retort through which the liquid is also forced, said retort being provided with baffle-plates and a draw-off cock, a steam-injector fitted to said draw-off cock, a second heating-coil in connection with the retort, an expansion-chamber connected with one end thereof, a condenser in connection therewith, and a gas holder or other receptacle.

2. In an apparatus for the continuous distillation of oil, a supply-tank, means for heating the same, a heating-coil comprising a series of pipes D, blocks E, incasing the same, removable covers closing and connecting the ends of the pipes, said pipes D gradually increasing in diameter from the inlet to the outlet, connections between this heating-coil and the supply-tank, a pump or equivalent device located between the two for forcing the oil through the heating-coil, a retort in connection therewith, a steam jet or blast attached to the heating-coil, a draw-off cock attached to the retort, a steam-ejector fitted to said cock, and a condenser in connection with the retort.

3. In an apparatus for the continuous distillation of oil, a supply-tank, means for heating the same, a heating-coil comprising a series of pipes, blocks of cast-iron or refractory material incasing the same, and removable covers closing and connecting the ends of the pipes, connections between said tank and coil, a pump or equivalent device located between the two, a retort in connection therewith, a draw-off cock for said retort, and a condenser in connection with the retort.

4. In the herein-described apparatus, the combination, with the retort and condenser of a dome R, attached to the retort, having an annular cup at its base, and a pipe connection between the upper part of said dome and the condenser and having a contracted portion, substantially as described.

Carl Maria Pielsticker.

Witnesses: Walter Joseph Norwood, Tom Francis Barnes, T. F. Barnes, all of 17 Gracechurch Street, London, E. C.

[fol. 1001] PETITIONER'S EXHIBIT No. 135.

J. S. LANG.

APPARATUS FOR DISTILLING HYDROCARBON OILS.

APPLICATION FILED APR. 2, 1909.

954,575. Patented Apr. 12, 1910.

2 SHEETS—SHEET 1.

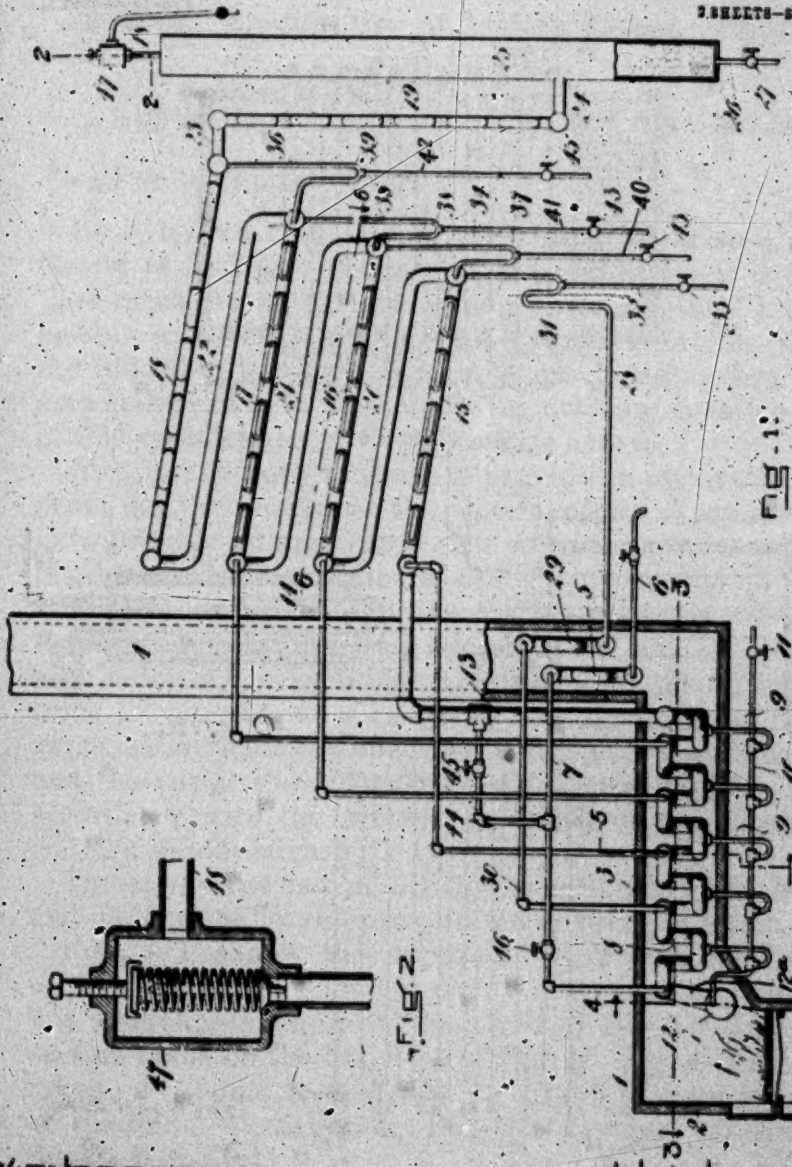


FIG. 1.

FIG. 2.

WITNESSES:
M. E. Flaherty
W. P. O'Brien

INVENTOR:
James S. Lang
by his attys
Church Rossmore & Church

4256

[fol. 1002]

J. S. LANG.

APPARATUS FOR DISTILLING HYDROCARBON OILS.

APPLICATION FILED APR. 2, 1909.

954,575. Patented Apr. 12, 1910.

2 SHEETS—SHEET 2.

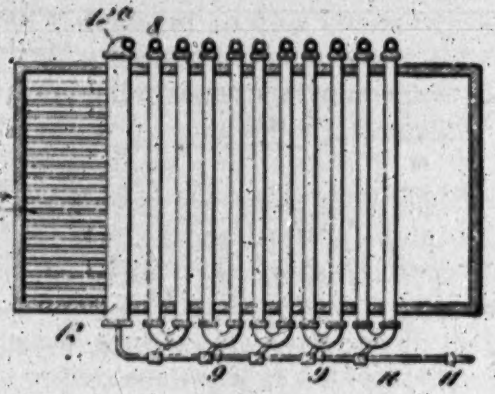


Fig. 3.

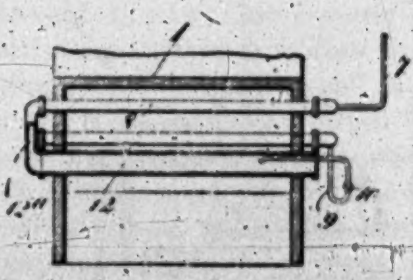


Fig. 4.

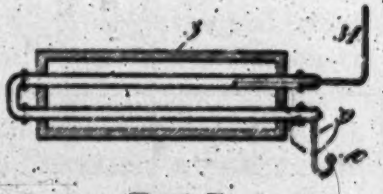


Fig. 5.

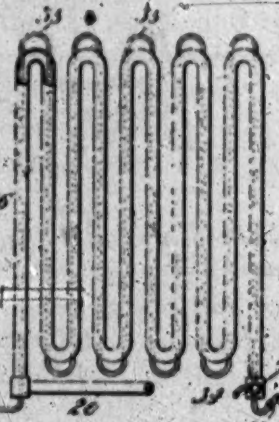


Fig. 6.

WITNESSES:

INVENTOR:

James S. Lang
by his attys
Clarke Raymond & Coulter

[fol. 1003] United States Patent Office

James S. Lang, of Boston, Massachusetts

Apparatus for Distilling Hydrocarbon Oils

954,575. Specification of Letters Patent. Patented Apr. 12, 1910

Application filed April 2, 1909. Serial No. 487,541

To all whom it may concern:

Be it known that I, James S. Lang, of Boston, in the county of Suffolk and State of Massachusetts, a citizen of the United States, have invented a new and useful Improvement in Apparatus for Distilling Hydrocarbon Oils, of which the following is a full, clear, and exact description, reference being had to the accompanying drawing, forming a part of this specification, in explaining its nature.

Although it is my purpose to provide an apparatus of the above entitled character, the especial object of my invention is to provide an apparatus embodying means for effecting the destructive distillation of crude hydrocarbon oil for obtaining as an ultimate product a hydrocarbon oil of predetermined volatility and especially an oil of relatively high volatility or such high volatility that the oil will continue to vaporize at a relatively low temperature or that vaporization will continue when the oil is contained in snow and the vapor therefrom burned for melting the snow in accordance with the process described in my patent, No. 863,855, dated August 20, 1907.

The apparatus embodying my invention can best be seen and understood by reference to the drawing in which—

Figure 1 shows the apparatus diagrammatically and mainly in side elevation but partly in vertical section. Fig. 2 is a section taken on the line 2—2 of Fig. 1. Fig. 3 is a section taken on the line 3—3 of Fig. 1. Fig. 4 is a section taken on the line 4—4 of Fig. 1. Fig. 5 is a section taken on the line 5—5 of Fig. 1. Fig. 6 is a section taken on the line 6—6 of Fig. 1.

Before referring to the apparatus, however, it should be understood that at a given pressure the lower the volatility of a hydrocarbon oil the higher the temperature at which

it will condense on which account the condensed oil will only give off vapor or an appreciable amount of vapor at a relatively high temperature. On the other hand, the higher the volatility of the oil the lower the temperature at which it will condense; in other words, the lower will be the temperature it takes to overcome its volatility. Consequently the condensed oil of high volatility will volatilize or give off an appreciable amount of vapor at a relatively low temperature. This principle I take advantage of in the apparatus constituting my invention and to which detailed reference will now be made.

Referring to the drawings, 1 represents a furnace. This furnace in so far as it is necessary to go into a description of the construction thereof, comprises a body portion 2 in which fuel is burned for generating heat, a relatively long-extending combustion chamber 3 through which the products of combustion are directed to pass, and a stack 4 into and through which the products of combustion pass from the combustion chamber. Located within the stack at a point preferably near the base portion thereof is what may be termed a primary heating coil 5. It is into this coil or primary heater that the crude hydrocarbon oil is first introduced to become vaporized therein by the heat products within and passing through the stack. The oil is led into the coil by way of an inlet pipe 6 and is preferably introduced under pressure.

Extending from the primary heater is an outlet pipe 7 which connects with the forward end of what may be termed a secondary or super-heater 8 located within the combustion chamber. This heater comprises a series of coils extending laterally back and forth to progress through the combustion chamber. The vaporized oil is introduced into the secondary heater from the primary heater by the way of the pipe 7 and as the vapor passes through the coils of the secondary heater it is subjected to a destructive distillation by the heat products within and passing through the combustion chamber. Owing to the fact that the secondary heater presents both a narrow and a somewhat extended passage the heat within the combustion chamber has full opportunity to effect such proper destructive distillation of the vaporized oil as may be desired to be obtained.

During the process of distillation undergone in the secondary heater the distillate as it passes off may leave a

deposit or residue within the coils of the heater of a tarry nature. For the purpose of taking care of this tarry substance there connect with the heater at different sectional points throughout the same waste pipes 9 extending downwardly and connecting with a common pipe 10 through which the matter may be drawn off upon opening a cock 11 located within this pipe. I prefer, however, that the tarry matter or residue may be led back into a retort 12 located [fol. 1004] within the combustion chamber at a point in front of the secondary heater or where it may be subjected to the direct influence of the heat from the burning fuel which will act to effect its further reduction. The deposit or residue will tend to work back into this retort from the pipe 10 since the chamber of the retort is located at a point below the coils of the secondary heater, the oil flowing into the retort tending simply to seek its level. In this connection also I would call attention to the fact that each of the waste pipes 9 is bent downwardly below the common pipe 10 before making its connection therewith, thereby forming a trap and preventing the entry or return of vapor through the pipe. Oil vaporizing in the retort 12 will pass directly to the secondary heater by way of the connecting pipe 12ª.

Extending from the rear end coil of the secondary heater is a pipe 13 connecting with a condenser 14. This condenser comprises a series of coils 15, 16, 17, 18 and 19 and it is with the bottom coil 15 that the pipe 13 connects. These coils of the condenser are progressively arranged one above the other and occupy an inclined position with the exception that the coil 19 has preferably a vertical disposition to facilitate the application of water for cooling this pipe should such application be deemed desirable. The respective coils of pipes are severally connected, the bottom end of the coil 15 being connected with the top end of the coil 16 by a connecting pipe 20, the bottom end of the coil 16 being connected with the top end of the coil 17 by a connecting pipe 21, the bottom end of the coil 17 being connected with the top end of the coil 18 by a connecting pipe 22, and the bottom end of the coil 18 being connected with the top end of the coil 19 by a pipe 23. The pipe 19 connects at the bottom end thereof by a pipe connection 24 with a pipe receptacle 25 which receives the oil condensing in the coil 19. From the pipe receptacle 25 the oil may be drawn off, as occasion may require, through a draw-off pipe 26 controlled by a cock 27.

It will be understood that the vapor passing over from the secondary heater may condense in any one of the coils of the condenser depending upon the relative degree of volatility of the vapor passing through the respective coils. Some of the vapor having a relatively low degree of volatility will be condensed at a relatively high temperature and accordingly may condense in the first coil, or the coil 15, of the condenser. Vapor of slightly higher volatility will condense in the coil 16 of the condenser, or that coil in which the vapor will have cooled to a slightly lower degree of temperature than in the coil 15. In the same way vapor of a relatively increasing degree of volatility will condense in any one of the remaining coils of the condenser depending upon the degree of its volatility. Vapor of a relatively high degree of volatility will condense in the coil 19 and the condensed oil from this vapor is the oil I desire to obtain.

It is the ultimate object of my invention to secure only an oil of relatively high volatility or such oil as will condense only in the coil 19. I have accordingly provided means whereby oil condensed in any one of the coils 15, 16, 17 or 18 may be conveyed back to the secondary heater and there subjected to a further destructive distillation tending to reduce this oil to such condition that the distillate will be of a sufficiently higher volatility to condense only in the coil 19. For this purpose there extends from the bottom end of the coil 15 a return pipe 28. This pipe connects with the coil 29 located in the stack of the furnace and thence with the secondary heater by a pipe 30. The coil 29, which forms a section of this return pipe, is located within the stack for the purpose of vaporizing the oil that may condense in the coil 15 of the condenser so that it may ultimately return to the secondary heater as vapor. Attention is also directed to the fact that the pipe 28 is bent at the point 31 to form a trap, some oil constantly remaining in this trap to prevent the entry or re-entry of vapor through the return pipe.

Should it be desired to obtain some of the oil condensing in the coil 15, arrangement is made whereby this may be done by means of a draw-off pipe 32 connecting with the return pipe at the point of the trap formed therein, this draw-off pipe being controlled by a cock 33.

Inasmuch as the oil condensing in the coil 15 or the first coil of the condenser is an oil of low volatility, as it con-

denses at a relatively high temperature, it is necessary that the vapor from this oil should be subjected to a considerable degree of destructive distillation before the distillate will be reduced to a condition of high volatility or where it will condense in the last coil of the condenser and there be secured an oil of high volatility which is the oil I desire to obtain. On this account the part 30 of the return pipe, which connects with the secondary heater, connects with it at a sectional point near the front end of the heater so that the vapor entering the heater at this point will pass through the major portion of the heater in order that the proper destructive reduction of the oil may be obtained by reason of the protracted period of destructive distillation to which the vapor will necessarily be subjected. Connecting also with the secondary heater are return pipes from each one of the other coils of the condenser for returning oil that may condense in these coils, with the exception of [fol. 1005] the last coil 19, the oil condensing therein escaping, as before described, into the receptacle 25 from which it may be drawn off. These return pipes are numbered 34, 35 and 36, respectively, the pipe 34 returning to the secondary heater from the bottom end of the coil 16, the pipe 35 from the bottom end of the coil 17 and the pipe 36 from the bottom end of the coil 18. In order that the oil returning through these respective pipes may be vaporized before entering the secondary heater I have provided for such vaporization of the oil by directing each pipe to return through a coil of the condenser below and next to the coil from which the pipe extends. As before described, the coils of the condenser are successively or progressively arranged, one above the other, and not only are they inclined so that oil condensing in each coil will flow to the bottom end thereof, but the coils are so far separated one above the other that oil returning from the bottom end of one coil may flow back through the return pipe passing through the adjacent coil, the oil tending simply to seek its level. Now as the oil passes through that portion of the return pipe contained in the coil below and adjacent to the coil of the condenser from which the oil is returning it will be subjected to a higher degree of temperature from the vapor within this pipe than the temperature within the coil from which it returns. In other words, the temperature in the coil through which the return pipe extends will be so high as to vaporize the oil contained within the

return pipe so that it may ultimately return to the secondary heater in the form of vapor prior to its further reduction.

In connection with the return pipes 34, 35 and 36 attention is directed to the fact that these pipes connect with the secondary heater at different sectional points dependent upon the relative degree of volatility of the oil or vapor returning through the pipes. In other words, the oil condensing in the pipe 16 returning through the return pipe 34 will be of a lower degree of volatility than the oil condensing in the coil 17 and the oil condensing in this coil in turn will be of lower volatility than that condensing in and returning from the coil 18. Accordingly the respective return pipes connect with the secondary heater at such points that the return vapor may be subjected to a greater or less degree of destructive distillation dependent upon the degree of its volatility when it enters the secondary heater. The pipe 34 returning from the coil 16 connects accordingly with the secondary heater at a sectional point some distance removed from the end of the heater and just forward of the point where the pipe 30, returning from the coil 15, connects with the heater. The pipe 35 returning from the coil 17 will connect with the heater at a sectional point just forward of where the pipe 34 connects therewith but nearer the end of the heater, while the pipe 36 connects with the heater at a sectional point still nearer the end thereof inasmuch as the oil returning through this pipe has almost the requisite degree of volatility and so need be subjected to but slight further destructive distillation in order to obtain its proper reduction. In further connection with the return pipes 34, 35 and 36 it is to be observed that each one of these pipes is bent to form a trap, the pipe 34 being bent to form the trap 37, the pipe 35 to form the trap 38 and the pipe 36 to form the trap 39. These traps by the oil remaining in them prevent the entry or re-entry of vapor through the respective pipes.

It may be desired to draw off oil condensed in any one of the coils 16, 17 or 18, and provision is made for doing this by the draw-off pipes 40, 41 and 42 connecting respectively with the return pipes from the respective coils at the points of the traps formed therein, each of the draw-off pipes being controlled by a cock 43.

It is sometimes found necessary or desirable to use a crude oil in the apparatus, which is of a very complex

nature. In other words, the crude oil contains oils of a highly volatile nature which if subjected to a degree of temperature more than sufficient to vaporize them would be converted into gas. I have accordingly provided in the apparatus shown means whereby when treating crude oil of the above character the oil may only be vaporized and sent directly to the condenser without being subjected to any destructive distillation. The highly volatile oils in the crude oil thus vaporized will be condensed and that portion of the oil condensing in the last coil of the condenser may be drawn off and saved in the manner described above. The remaining oil condensnig in the condenser will be returned to the secondary heater from that portion of the condenser in which it may be condensed, and in the secondary heater will be subjected to such destructive distillation as will secure its proper reduction.

The means I have provided for primarily preventing the destructive distillation of the crude oil in question is the pipe 44 interposed between the pipe 7, which connects the primary heater or vaporizer with the secondary heater, and the pipe 13 which joins the end of the secondary heater to the condenser. In this auxiliary connecting pipe 44 is located a valve 45. A valve 46 is also located in the pipe 7 beyond the point where the pipe 44 connects therewith, with the effect that by closing the valve 46 and opening the valve 45 the oil vaporized in the primary heater will pass directly to the condenser.

When oil is treated that does not contain oils of a rela- [fol. 1006] tively high degree of volatility and which needs primarily a destructive distillation then the valve 45 is closed and the valve 46 opened by which means the oil vaporized in the primary heater will pass directly to the secondary heater.

Inasmuch as it is not my purpose to obtain gas as an ultimate product through the destructive distillation of oil treated in the apparatus, it is not necessary to subject the oil in the secondary heater to any extreme degree of heat, a normal fire only being maintained in the furnace. Though precautions may be taken to prevent an excessive heating of the oil and its conversion into gas, yet gas may form in the apparatus. I have arranged to take care of this gas by providing an escape valve 47. This valve may be any one of a number of well known varieties and is preferably arranged in the top of the receptacle. The valve 47 is so set

as to allow the gas to escape through the valve and the pipe 48 connecting with it, when the pressure of gas within the system reaches a determinate degree of compression above the pressure normally maintained therein. The gas so escaping may be saved or it may be conveyed back into the body of the furnace and burned.

The operation of the apparatus is briefly as follows: Crude oil preferably under pressure is introduced by way of an inlet pipe 6 into the primary heating coil 5 where it becomes vaporized. Thence the vapor passes by way of an inlet pipe 7 to the secondary or super-heater 8 where the vapor is subjected to a destructive distillation. Any oil or tarry matter that may collect in the secondary heater may be drawn off by way of the waste pipes 9 and connecting pipe 10 upon opening the cock 11 located in the pipe 10 or by closing this cock the tarry matter may be conveyed back to a retort 12 where the oily product may become vaporized and again pass by the way of the pipe 12ª into the secondary heater. The vapor having undergone a destructive distillation in the secondary heater will pass out of this heater by way of the pipe 13 to the condenser 14 and will pass through the several coils 15, 16, 17 and 18 of the condenser to a coil 19, that is, if the vapor is of sufficiently high volatility. Vapor condensing in the coil 19 passes over by way of the connecting pipe 24 to a receptacle 25 where the condensed vapor or oil may be drawn off. Oil condensing in the primary coil 15 of the condenser is conveyed back by way of a return pipe 28 to a vaporizing coil 29 arranged in the stack whence the vapor returns by way of the pipe 30 to the secondary heater. If desired, oil condensing in the coil 15 of the condenser may be drawn off by way of a pipe 32. Oil condensing in any one of the pipes 16, 17 or 18 of the condenser is returned to the secondary heater at different sectional points therein by the respective return pipes 34, 35 and 36, these pipes passing in turn through the coil of the condenser next adjacent to the coil from which they return on which account the returning oil will become vaporized before entering the secondary heater. In case it is desired to obtain oil condensing in any one of the coils 16, 17 or 18 of the condenser such may be obtained by drawing it off by way of the draw-off pipes 40, 41 and 42 connecting with the respective coils of the condenser, each pipe being controlled by a cock 43.

If by reason of the nature of the oil it is not thought desirable to subject the oil to destructive distillation in the secondary heater the vapor from this oil produced in the primary heater may be led directly to the condenser by way of the outlet pipe 7 and connecting pipe 44, the valve 45 being opened and the valve 46 being closed. Ordinarily in the operation of the apparatus the valve 45 will be closed and the valve 46 opened, that is, when an oil is being used which it is desired to subject not only to the influence of the primary heater, but also to the influence of destructive distillation in the secondary heater. In case gas is formed in the apparatus this gas may escape through an escape valve 47 arranged in the top of the standpipe or receptacle 25, that is, when the gas reaches a degree of compression sufficient to open the valve.

Having thus fully described my invention, I claim and desire to secure by Letters Patent of the United States:

1. In an apparatus of the character specified, the combination of a furnace, a heater comprising a series of coils progressively arranged, a condenser comprising a series of coils also progressively arranged, and return pipes from said condenser to said heater, said pipes connecting with the coils of said condenser for returning the oil condensing therein to said heater and which coils connect with said condenser and return to connect with said heater at sectional points relatively commensurate with the order of progression of their respective coils.

2. In an apparatus of the character specified, the combination of a furnace, a heater comprising a series of coils progressively arranged, a condenser comprising a series of coils also progressively arranged, return pipes from said condenser to said heater, said pipes connecting with the coils of said condenser for returning the oil condensing therein to said heater and which coils connect with said condenser and return to connect with said heater at sectional points relatively commensurate with the order of progression of their respective coils, and means whereby [fol. 1007] the oil returning through said pipes may be vaporized before entering said heater.

3. In an apparatus of the character specified, the combination of a furnace having a combustion chamber a heater located in said combustion chamber, the heater comprising

a series of coils progressively arranged, an auxiliary retort located within said chamber, and drain pipes connecting with said heater at sectional intervals therein and which connect with to empty into said retort for returning to said retort the tarry residue that may accumulate in said heater, each of said pipes being bent to form a trap.

4. In an apparatus of the character specified, the combination of a furnace having a combustion chamber and stack rising from said chamber, a primary heater, means whereby oil may be introduced into said primary heater, a secondary heater located in said combustion chamber, a connection between said primary and secondary heaters, a condenser of sectional character with which said secondary heater connects, a return pipe extending from the primary section of said condenser and returning to said secondary heater, said return pipe comprising in part a connection subjected to the heat from said furnace, and a series of return pipes extending from said condenser at different sectional points therein to connect with said secondary heater, each of which pipes is arranged to return through a section of the condenser in which the vapor therein during the operation of the apparatus is at a higher temperature than the vapor in that section of the condenser from which the pipe returns.

5. In an apparatus of the character specified, the combination of a furnace, a primary heater, means through which oil is introduced into said heater, a secondary heater, a connection between said heaters, a condenser, a connection between said secondary heater and condenser, means whereby a direct connection may be had between said primary heater and condenser, and a series of return pipes between said condenser and said secondary heater whereby vapor condensing at different sectional points therein may be returned to said secondary heater.

6. In an apparatus of the character specified the combination of a heater and a condenser with which said heater connects, return pipes from said condenser to said heater, said pipes connecting with said condenser at different sectional points thereof for returning oil condensing therein to said heater, each of said pipes returning through a portion of the condenser in which the vapor therein during the operation of the apparatus is at a higher temperature

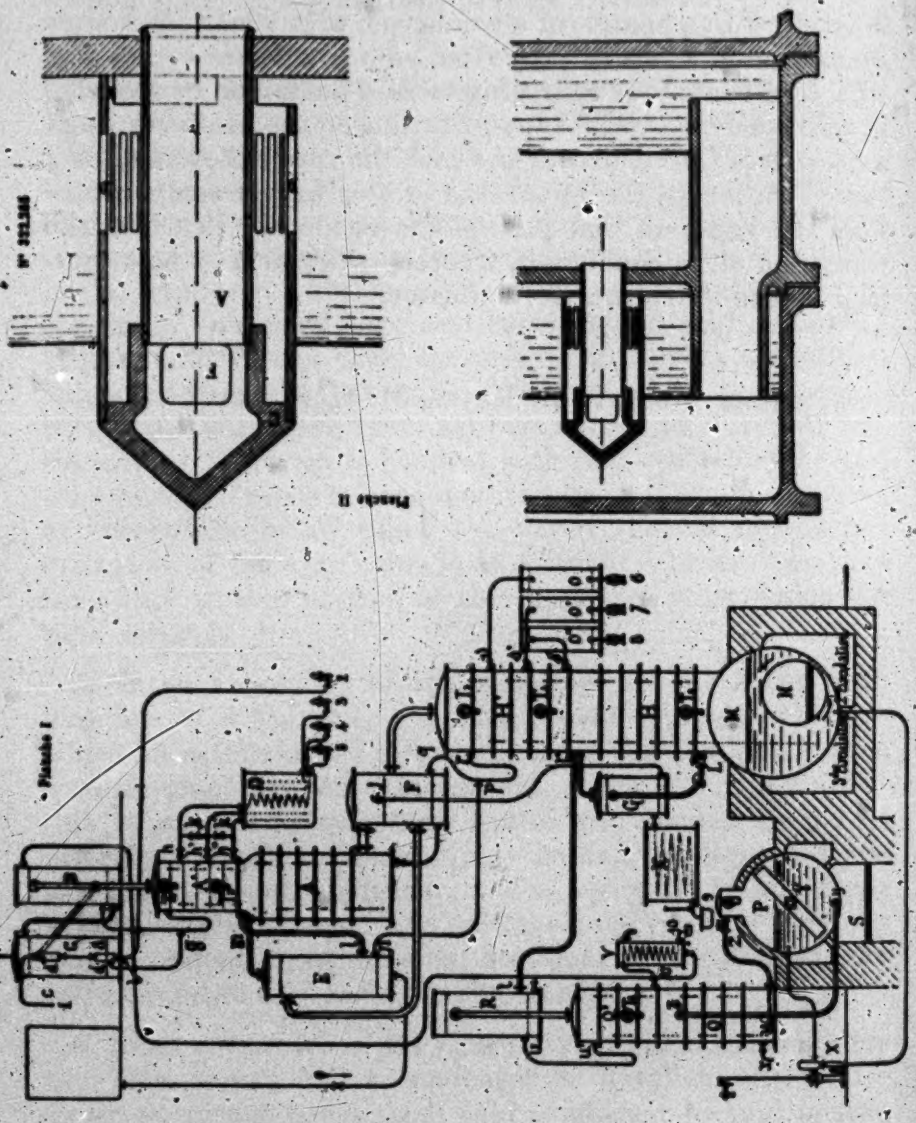
than the vapor in that section of the condenser from which the pipe returns and which pipes conneet respectively with the heater at different sectional points from the end of said heater.

7. In an apparatus of the character specified, the combination with a heater, of a condenser with which the heater connects and a return pipe from said condenser connecting with said heater for returning to said heater oil condensing in said condenser, said pipe returning to the heater through a portion of the condenser in which the vapor therein during the operation of the apparatus is at a higher temperature than the vapor in that part of the condenser in which the returning oil is condensed, whereby said oil may be vaporized before its return to the heater.

James S. Lang.

Witnesses: John E. R. Hayes, M. E. Flaherty.

[fol. 1008] PETITIONER'S EXHIBIT No. 136



[fol. 1009] TRANSLATION OF PETITIONER'S EXHIBIT No. 136

French Republic, National Office of Industrial Property

Patent of Invention of June 2, 1902

XV.—Lighting, Heating and Refrigeration. No. 322,265

3.—Combustibles and Apparatus for Heating

Patent for 15 years, applied for June 7, 1902, by Mr. Barbet (Emile-Augustin), for a process and apparatus for the continuous rectification of petroleum and volatile hydrocarbons

(Granted September 30, 1902. Published Jan. 31, 1903)

The rectification of crude petroleum is done generally in an intermittent manner, in successive charges in large boilers. In some works a battery of boilers is used, placed at descending levels and a sort of continuity of rectification is realized; the four first boilers furnish essences of petroleum (petroleum ethers, benzine, naphtha), the following boilers the lighting petroleum, and the last the paraffin oils. The crude petroleum circulates in an uninterrupted manner from one boiler to another and when it leaves the last, it is led into special boilers called "black pots" destined to provoke a supplementary fractionation of illuminating oil.

The mode of working is subject to a certain number of criticisms.

First, the boiling in a large boiler of the very complex liquid is incapable of giving anything else than a distillate itself very complex. Then for each of the fractionating boilers instead of obtaining a definite product of a chemical compositions which differentiates the products of two neighboring boilers, one has nothing but a mixture of hydrocarbons of which the mean boiling point may without doubt obey a certain law of relative progression from one boiler [fol. 1010] to the other, but it is still a heterogeneous mixture. But industry always prefers simple and definite products.

To succeed in making a true cut or a complete assortment of the manifold components of crude petroleum, recourse

must *must* be had to fractionating processes similar to those which are employed for the distillation of alcohol. Everyone knows that the distillation of a crude alcoholic liquid in a simple alembic is incapable of giving a fractionated distillate. The separation of the light products in one part, then of the alcohol strictly speaking, and finally of the heavy products and of the water can not be done in a manner sufficiently complete and clear cut, except by the employment of rectifying columns with plates surmounted by condensers. We have demonstrated finally that the analysis of the products is not made in the condenser, but that the liquid condensed and thrownback acts as a valve and produces the division into lots of the various products in successive stages of the plate columns. The superposed plates constitute, so to speak, classifying valves of an "alcohol bolting room," and in certain stages, if liquid is withdrawn from a plate it is found to be a perfectly defined and suitable composition, if the working of the apparatus is itself correspondingly regulated.

It cannot be otherwise with the petroleums, with this advantage, that the boiling points of the various components are very distinct and consequently the separation will be easier to make. One must, moreover, in the adaptation of the process of continuous rectification of alcohols to petroleums, not lose sight that there are many more different cuts to fractionate than in the distillation of alcohol.

Plate 1 represnts the apparatus which we have devised to carry out the program which we are going to define. Crude petroleum is pumped into a tank, placed at an upper stage and from there enters at the bottom of a tubular boiler E before entering the essence purifier, A. In descending from plate to plate, the crude petroleum is methodically freed of its essence; the vapor which is finally set free at the feeding plate is already better "fractionated" than through a large boiler, thanks to the method, but nevertheless this vapor entrains some too heavy products or lighting oils.

Also we have disposed below A a certain number of plates A', then a water condenser B and a cooler C. Except for some uncondensable gases (cymogene, rhigolene) all of the vapors are liquified. The gases leave by a tube *c*. (Outlet No. 1) and they are sent to the furnace for burning.

[fol. 1011] The more volatile essences chilled in C leave by the tube *b* and go to the gauge glass 2. At the entrance of this gauge glass is found a precision valve which permits the regulation in an invariable manner of the proportion of essence which one wishes to let pass. This proportion depends upon the composition of the crude petroleum. For regulating it, one depends upon the indications of a densimeter such as on those of the dial thermometer T_1 placed in the upper part of the plates A'.

All of the excess of essence is forced to redescend by tubes *a g* to mix with the reflux of B and to re-enter the purifier A'.

In A' this liquid is subjected to boiling of such sort that more volatile essences are re-evolved into vapor. Thus the liquids of the plates are freed of dangerous essences, and, if in *h* an extraction of from 2 to 4% of liquid is made, there is received at the gauge glass 5, after chilling in D, a redistilled essence, of which the boiling point is not high and of which the composition is very simple. If this product be redistilled, scarcely any rise in temperature will be found between the commencement and end of distillation.

An extraction can be made equally well two plates lower in *h'*, then two plates still lower in *h''*. One will receive in the gauge glasses 4 and 3 liquids well homogeneous and presenting between them distinct differences of density and boiling range. One can, if one finds it of interest, multiply the assortment; each stage will furnish a liquid which can have its special destination in industry.

Let us remark, in passing, that all of these liquid extracts are clear and proper because they come from condensed vapors and not from the crude petroleum.

On arrival at the base of A the crude petroleum has no more light essence. The point at which this will occur will depend directly upon the composition of the crude petroleum, upon the intensity of boiling, and the quantity of extractions effected in *h*, *h'* and *h''*. An illuminating petroleum can very well be drawn off in *h''*; all depends upon the manner of regulating the apparatus; whatever is desired can be made.

The purified crude petroleum passes into the tubular boiler F. This must produce sufficient petroleum vapor to operate all of the purifier. The heating vapors may per-

haps be live steam from a generator at six or eight atmospheres (kilos) pressure, or the vapor of illuminating petroleum leaving the top of the rectifier, properly called, H, H′.

[fol. 1012] The purified petroleum leaves the heater F in *j*. It reaches a temperature much higher in boiler G and enters at the feeding plate of column H. The methodical boiling on the succesisve plates of H provokes the total evaporation of all lighting oils, and even a little of the paraffin products. The separation of all of these vapors is produced on the plates H exactly according to the same law as at all times in the purifier. A water condenser and cooler can still be used to operate the reflux; it is preferred to use the vapors evolved in *h′* to heat first the boiler F, then the "petroleum heater" E. If some gases are formed, they escape by the tubes *l m* and go thus to reunite with the purifier A. If there is a small excess of vapors of illuminating petroleums not condensed in E they *do* by the same road into A′ where they will be stopped in passage by the liquid which re-descends on the plates.

The two refluxes from F and E, *q*, *r* and *u p*, re-enter onto the rectifier plates H′ where the components classify themselves by their order of volatility. In S and S′ and S‴ one will withdraw heavier and heavier lighting oils. These are cooled respectively in coolers O, O′, O″ and through the gauge glases 7 and 8 will be directed towards separate and appropriate reservoirs. The thermometers T_3, T_4, T_5, permit of knowing what passes, and the various extractions are regulated in such a manner as to obtain predetermined and constant temperatures in these different stages.

The heating of the column H, H′ is provided by a sheet metal direct fired boiler M, which can be of any desired form; cylindrical, horizontal or vertical with exterior or interior firing, etc.

On this boiler we take up in L a certain quantity of vapor for the boiler G, because we hold that the purified petroleums must be almost boiling, or even boiling, when it enters H in order that it may not arrest the illuminating oil vapors which are evolved on the plates H.

The boiler M which we have indicated is horizontal, cylindrical, with an eccentric interior furnace *n*. The object of this dissymetry is to set up in the boiler a circulating move-

ment of the liquid; the right wall of M is more heated than the left wall, because the right flue receives the second circulation of gas and not the third. The abundant bubbles of vapor which form in the restricted space between the walls of N and M form a current of liquid following the direction of the arrow. This rapid rotation will prevent deposits of solid matter and consequent overheating. We reserve to [fol. 1013] ourselves to assist the rotating movement of the liquid of the boiler by a mechanical agitator placed in the lower part of M.

The boiler M possesses a stock sufficient to enable the evaporation to be easily regulated, the intensity of which is indicated through the employment of a very sensitive manometer. The crude petroleum must there be completely free of that which pre-existed as illuminating oil.

The boiling mass can be withdrawn in proportion by a pump X, to be sent to the old black pots. But we do not pretent to in addition, render continuous the operation of the complementary roasting which succeeds, by cracking, in furnishing further a certain contingent of illuminating oil.

Let us suppose another horizontal cylindrical boiler P provided with an agitator with blades Y; the boiler is of thick plate, of a make capable of supporting five or six atmospheres pressure. The pump X forces the exhausted crude petroleum into the boiler P. Due to the agitator and to the pressure, the cracking is produced more quickly than in the black pots at atmospheric pressure. The valve Z is partly open and is regulated to direct the vapors to the bottom of the plate column Q Q'. At the same time, the emptying valve Y is regulated in such a manner as to cause the liquid to rise (due to the pressure) up to *z*. In this neighborhood, the superheated liquid is transformed partially into vapor, which rises in the plates Q', and by the fact of this expansion, the temperature falls. Also the agitator W can provoke anew the boiling of the paraffin residue and expel from it all that can be volatilized. The excess liquid, well exhausted by the action of W. departs through the valve *x* and is directed to the paraffin presses, or as well, according to circumstances, to the furnace to be burned.

The paraffin and illuminating vapors rise in the plates Q′; the cuts are made due to the refluxing from the condenser R. Evidently good care will be taken not to send cold water into the condenser R; it can be fed with hot water coming from B, and if hot water is lacking, the desired heating will be produced by a little direct injection of steam at the bottom of R. It will suffice in effect not to permit the paraffin to solidify in the tubular chamber.

The illuminating vapors leave the condenser R by the tubulature *t* and by the tubes *tt′*, go to the column HH′ where they are refined and classified; the paraffin liquids condensed run back by *uu′*, they are freed in Q′ of all illu- [fol. 1014] minating products and leave in *v* to be partially cooled in V. The same observation as for R; the water of V must be maintained at least at 70° to prevent all solidification of paraffin. The latter leaves in 10 and is directed to special containers to be bleached and purified.

We have said that the auxiliary boiler B receives its heat from the boiler M through the valve L. There is then a condensation in G. The liquid which is formed there leaves at the base of G and goes to be cooled advantageously in K. There also care will be taken to have sufficient temperature (through the injection of a little steam) so that no obstruction of paraffin or vaselin- can be produced. The condensed product leaves in 9 and can either be sold directly or returned to the process, for example, in the upper part of Q′.

It will be noted in short that we have taken account of a fractionation in ten different lots No. 1 to 10; but we repeat that as many different lots can be made at different temperatures as there are plates in the various columns; it is a commercial question.

We have spoken throughout of plate columns without saying how these plates are made. We give (plate II, fig. 2) an assembled section and fig. 3 a detail of the cap in half its actual size.

Let us assume some superposed cast iron fragments; in the plates are inserted the chimney A of a certain number of cast iron caps. The upper part of A is threaded, and covered with a sort of cast iron hat C with a conical head, which is threaded on A.

The petroleum vapor leaves through the orifice F. On another part another iron tube G is threaded on C. This

tube rests on the plate B by means of three or four feet E. Some long narrow windows D are cut in the tube G, in order to free the passage for petroleum vapors; but it is immediately noted that the bubbles of vapor are finely divided, in a manner to separate them well and to divide them in a liquid mass. It is the only logical manner of accomplishing intimate contact and consequently to make a rational assortment of the liquids according to their boiling temperatures.

The system of windowed caps which we have described can vary a little in its construction; one can in particular adopt the same form, in pressed steel, as for out comb-caps of the alcohol industry. The cap which we have sketched is indicated preferably for the use of large stocks of liquids [fol. 1015] on the plates. One can be assured that the boiling will have placed in emulsion even the deepest parts of the liquid layer. In place of being made of cast iron the caps can be of any other metal, copper, bronze, etc. It is, above all, the new form of these caps that we claim. C has a conical top in order that it cannot accumulate insoluble carbonaceous masses.

The use of our special caps will furnish the best results, but it goes without saying that we reserve the possibility of using all of the other systems of caps, which exist and even of making use of perforated plates.

In Resume, that which we claim above all in the present patent is the method and apparatus of continuous fractionation which we have described for crude petroleums, of whatever source they may be. We thus avoid the costly and dangerous boilers actually used. The crude petroleum passes very rapidly in the apparatus and there results very much less caramelization of the essential or illuminating products, which pre-existed in the crude petroleum, whence better yields. Our process will also give a great economy of combustible material and of more homogeneous and less dangerous commercial products. We intend, in effect, to have it noted that all of our fractions are "redistilled," and consequently freed of gas or very volatile elements which ordinarily provide facilities for ignition.

We claim more particularly in our apparatus combination, the manner in which we have organized the sequence of operations, and the heating of the first columns by means

of the uncondensed products of later columns of higher boiling point. We claim the use of several thermometers to serve as a basis for the regulation of the apparatus and to indicate the proportions which ought to be taken from each stage in view of the constancy of chemical composition of the various fractions.

We reserve to ourselves the right of using heating under pressure to assist the cracking of heavy oils as we have described.

And finally, we claim the use of windowed caps which we have described, caps which s-ould permit us to make column plates having a very great stock of liquid.

Paris, June 7, 1902.

E. A. Barbet.

N° 399.725 M. Barbet Pl. unique

Fig. 1

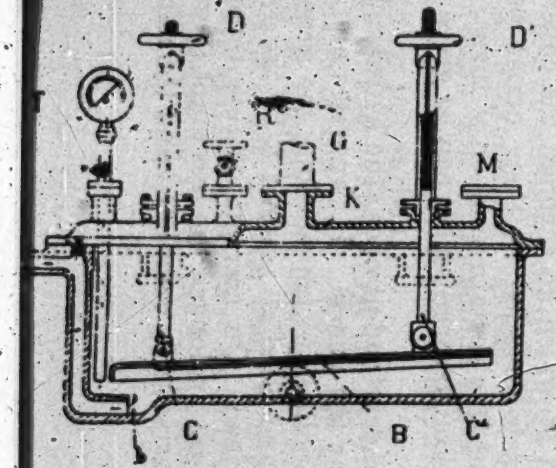


Fig. 2

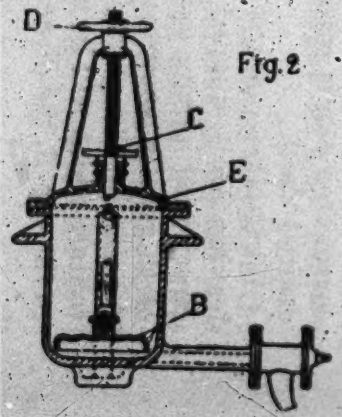
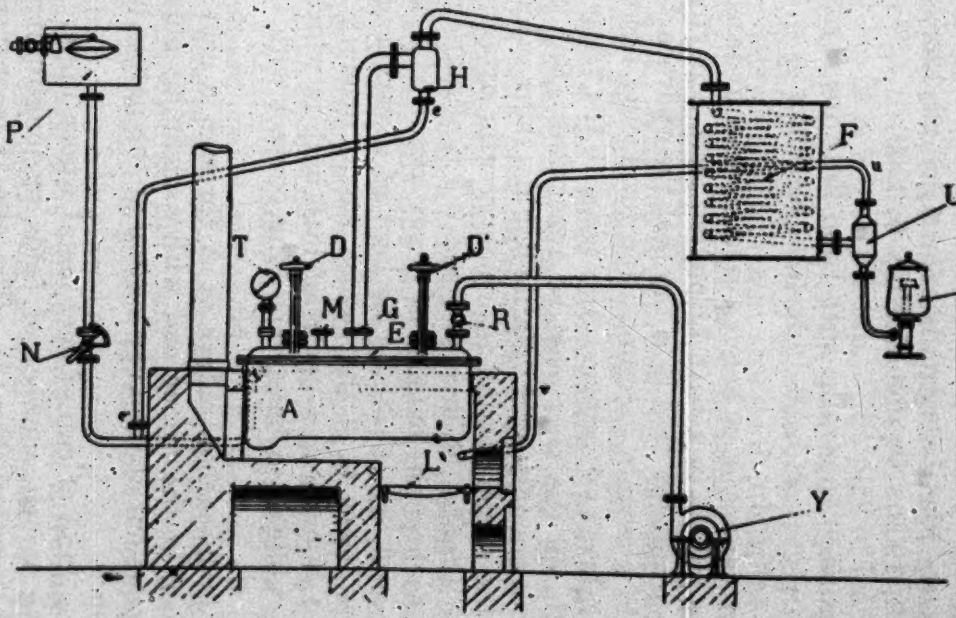


Fig. 3



[fol. 1017] TRANSLATION OF PETITIONER'S EXHIBIT No. 137

Translation of the French Patent No. 399,722, to Emile-Augustin Barbet. Applied for April 29, 1908. Granted May 1, 1909. Published July 6, 1909

Decomposing Apparatus with Lead Bath for Hydrocarbons and All Industrial Residues

When vapors of a heavy, vaseline-like hydrocarbon are made to bubble in a bath of melted lead, a partial dissociation is produced, that is to say that the hydrocarbon is subjected to a certain decomposition producing lighter hydrocarbons, tars and carbon. According to the temperature of the bath, oil gas may even be generated. But if it is desired to form only light volatile liquids, there is another factor of the decompostion to which greater attention should be paid, that is the duration and the thoroughness of contact of each of the bubbles of heavy vapor with the dis-ociating metal, which should be kept at a very regular temperature lower than that which would produce oil gas.

Fig. 1 shows a new model of lead bath in which the vapors are obliged to have very long contact with the melted lead.

The hydrocarbon enters at A through a cast iron pipe furnished at the upper end with a cleaning plus *a*. This pipe opens out at the very bottom of the pan in a small depression *b*.

B is a kind of cap of cast metal whose upper part comprises a certain number of folds or longitudinal grooves (see the section, Fig. 2). The cap B is suspended from two vertical rods C and C′ which go through the cover K of the pan and are screw-threaded at their upper part. By turning wheels D and D′ a certain number of turns, the corrugated pan is raised or lowered and it can be given the desired slant.

What takes place is understood at once: the hydrocarbon leaving Ab is stopped by the pan B. It vaporizes and the imprisoned vapors are obliged to travel along the grooves of B, greatly compress and piled up against B by the great density of the melted lead. On account of this through contact which will be more prolonged the less slant there is to the cap B, the disaccosiation is completed and the nature

[fol. 1018] of the products which result therefrom depends on the temperature given to the land bath and the speed of feed through the admissio*b* pipe.

The new suspensio*b* of the corrugated cap has another advantage: at the begin-ing when the cover is bolted into place, the cap B is left at the top. The pigs of lead previously placed on the bottom of the pan melt little by little. It is then that the cap is lowered while observing ex-erior marks for determining its slant and its depth in the lead.

When at the end of several days, the bath is to be opened, the wheels are actuated for li*g*ting the cap from the lead before it sets. Without this precaution, the cap would be held fast and the cover could not be removed.

Fig. 3 shows the whole decomposing apparatus. P is the regular tank for feeding the hydrocarbon: M is the regulating cock with graduated scale: L is the grate.

The disassociated vapors, before passing to the condenser F, go through a condensation box cooled by the surrounding air H: only the very heavy products which are sufficiently disassociated are condensed here. Those products return of themselves to the entrance of pipe A (pipe *e e'*) and thus render the lead bath to be dissociated.

In this way, only sufficiently light products of greater trade value are cooled in Condenser F, flowing off through gage X. These products can be treated with sulphuric acod for destroying olefines, thiophenes, etc., and they can then be sent to be rectified: The gases that cannot be condensed go through the pipe *u v* to grate L'.

In certain cases, it is advantageous to introduce at the same time as the heavy oil, a small proportion of water which will vaporize sim*lu*tancously and which can react by its own dissociation to modify the chemical composition of the hydrocarbon. It can be seen that the dissociation of the water will be efficacious above all when it is desired to decompose tars, for the latter, it might be said, contain nothing but carbon.

It will be noticed that the carbon liberated floats on the surface of the land. When the apparatus is opened it is easy to remove this superficial carbon and as it is always carried along a little lead, it should be burned independently in a flat crucible so as to recover the lead. It would be simpler to open the cover while the lead is still red;

the carbon will burn on the surface and when it has disappeared the dissociation process will be commenced again. [fol. 1019] Finally, without opening the cover, air can be sent to the surface of the lead bath for igniting the carbon and making burn to the end: the hand fan Y sends air through cock R and the closure M is opened. The flame goes out through M and when it no longer passes out, it is a sign that the operation is finished. R and M are closed again, and before injecting hydrocarbon, a little water is fed to the lead so that the vapors formed displace the air and make the explosions impossible.

This process of burning carbon formed, on the spot, offers great advantage, for without that the lead bath would be out of action for hours.

Summary:

Decomposing apparatus which has for the result great increase in duration of the contact of the heavy oils with the melted lead, for causing a more regular and complete decomposition, and for giving in short the maximum output in volatile liquids of important commercial value. This decomposing apparatus allows the slant of the cap to be modified at will, to immerse it or lift it from the lead without opening the cover. The parts not decomposed return automatically to the molten lead. Finally the carbon formed can be done away with by combustion with or without the cover, in such a way that the lead bath remains indefinitely in good condition of operation.

Tr. MMJ.
8-19-25.

[fol. 1020] PETITIONER'S EXHIBIT No. 138

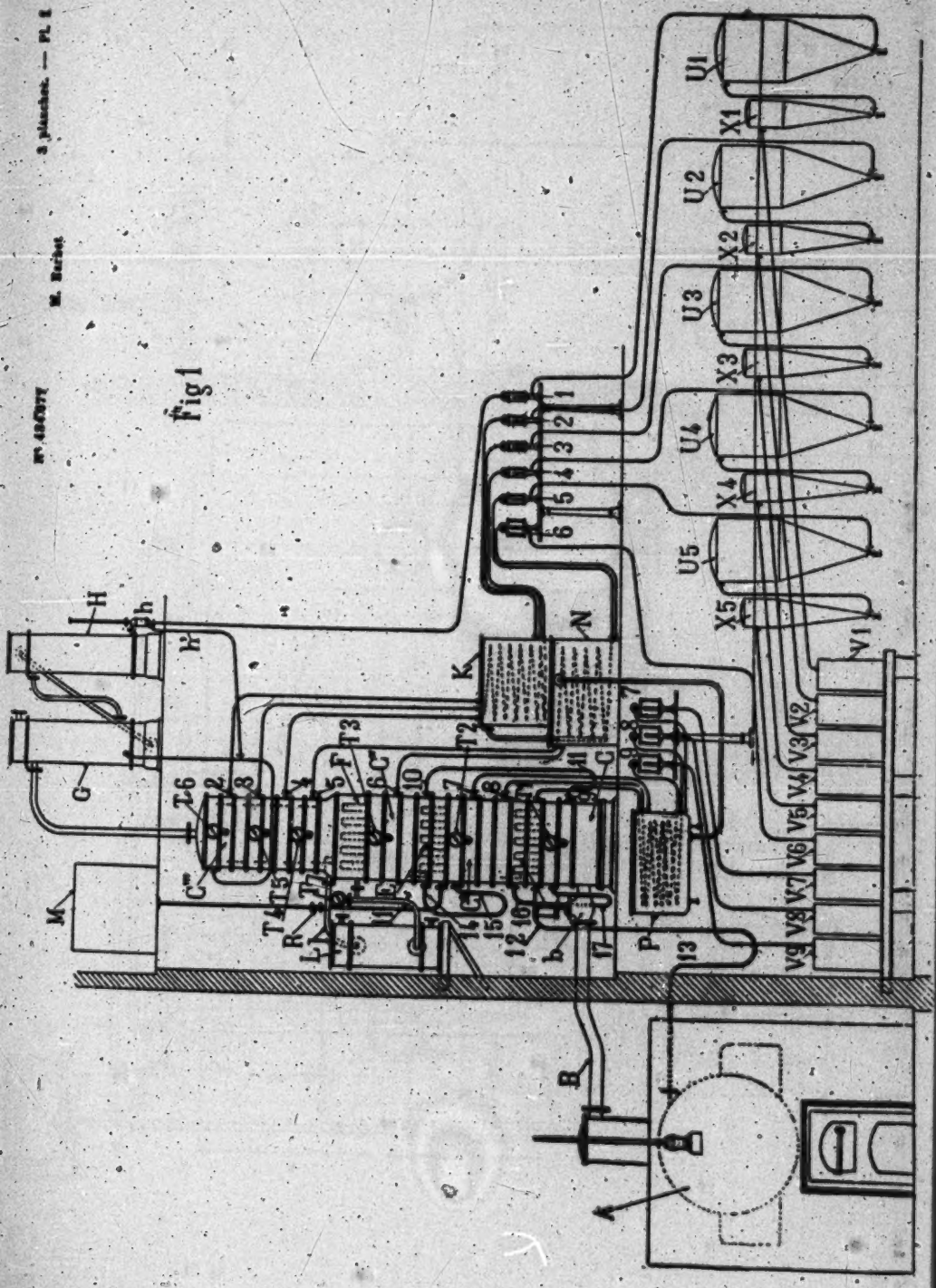


Fig 1

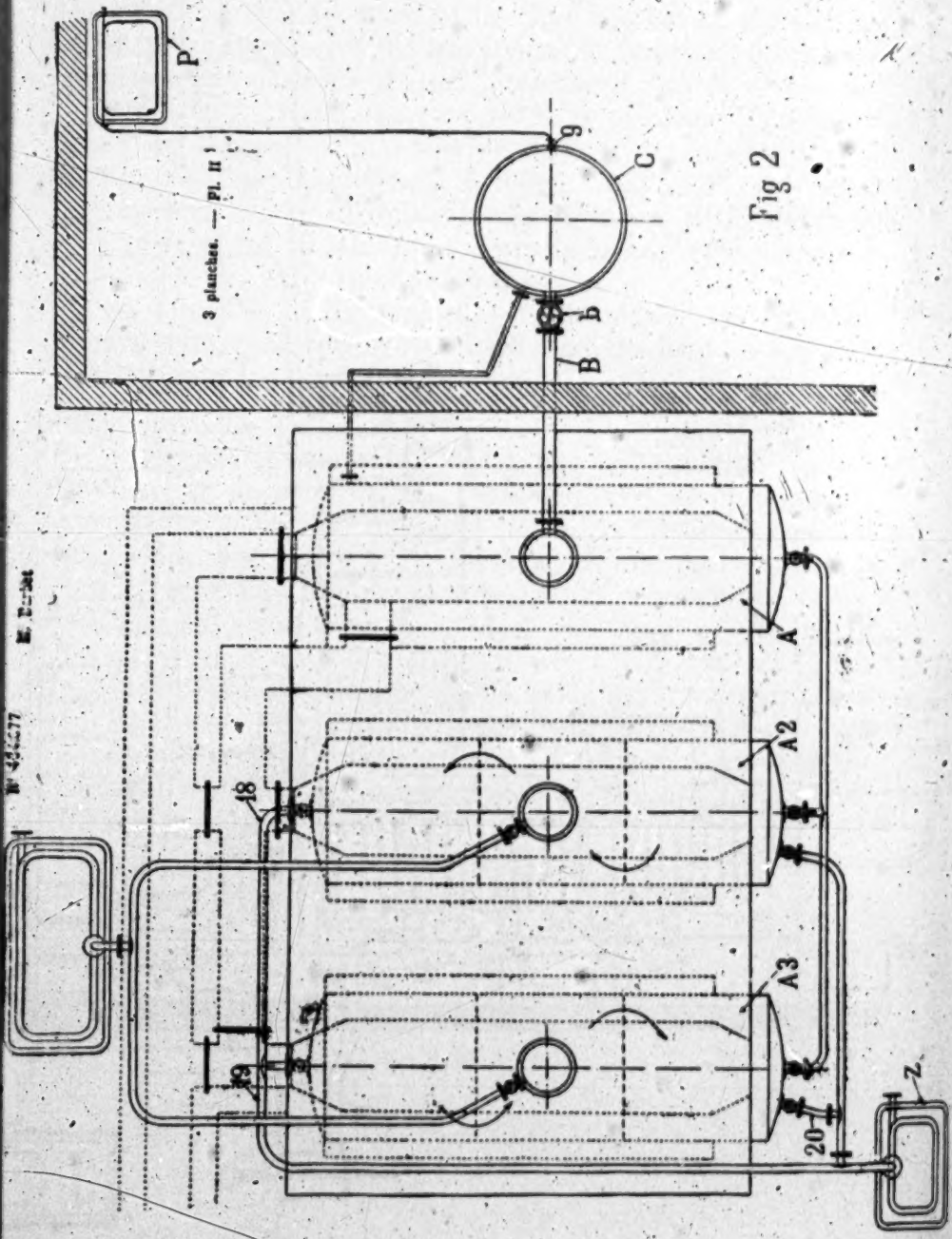
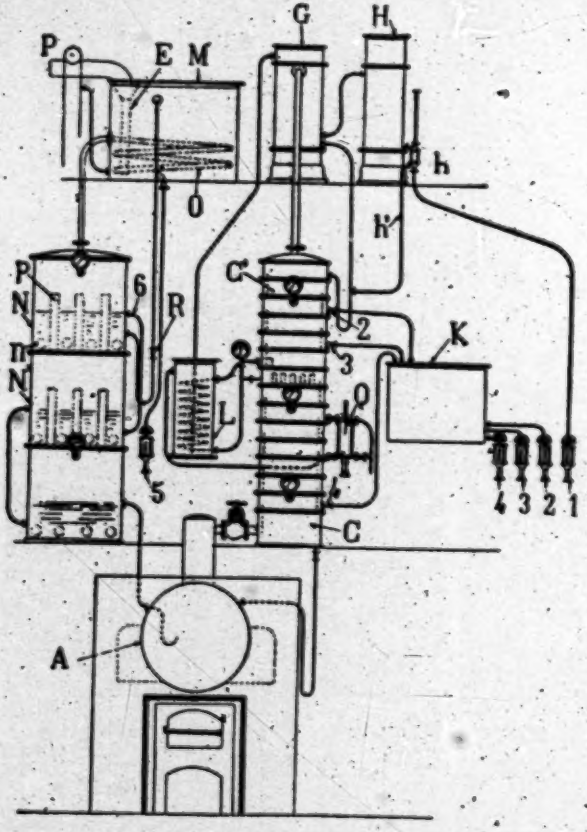


Fig 2

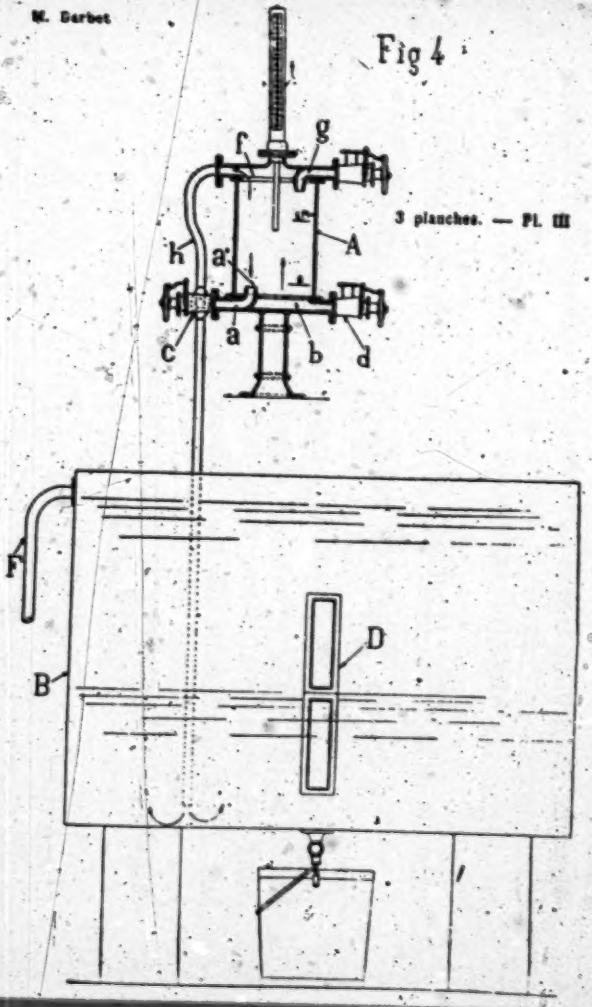
3 planches. — Pl. II

Fig 3.



M. Barbet

Fig 4.



3 planches. — Pl. III

[fol. 1022]

4283.

[fol. 1023] Translation of Petitioner's Exhibit No. 138

French Republic, National Office of Industrial Property

Patent of Invention. No. 434,677

XV—Lighting, Heating, Refrigeration, Ventilation

3—Solid, Liquid and Gaseous Combustibles

Simplified Apparatus for the Continuous Distillation and Purification of Crude Petroleum or Oil Tars

Mr. Emile-Augustin Barbet, Residing in France (Seine)

Applied for December 3, 1910. Patented December 4, 1911. Published February 9, 1912

(Patent of Invention of Which the Delivery Has Been Put Off in Execution of Art. 1187 of the Law of July 5, 1844, Modified by the Law of April 7, 1902)

In the first adaptations of the principles of continuous rectification to the purification of crude petroleums or to the distillation of oil tars, very complicated apparatus have been created, composed of three columns with successive plates or at least of two. This complication is useless and the separation of numerous volatile components of crude petroleum or of tars can be realized perfectly in a unitary plate column with a single heating, as that which is represented in figure 1. The number of plates itself is very limited, but at different heights are interposed internal condensers which, although very elementary, nevertheless play a preponderant role, which will be explained a little further on.

A is a large boiler heated by direct fire. It is surmounted by a dome which, through the tube B and the valve *b* sends the vapors, not directly to a condensing coil but to the base of the rectifying column C.

The heterogeneous vapors rise through the capped plates [fol. 1024] of the column C and arrive finally at the condenser D which keeps back a part of the less volatile vapors. A condensate forms, that is to say, a liquid which falls back onto the two or three capped plates of the base of the

column. This liquid of condensation thus finds itself subjected on the plates C to a new automatic, ebullition, which returns the volatile to vapor in such a way that if one goes to withdraw the reboiled liquid through the valve 9, one receives a product freed from the volatile elements, an illuminating petroleum well freed from benzine.

The vapors which have escaped condensation in passing D now comes to splash about in the liquid of the plates C' and this liquid itself results from a partial condensation produced in the second internal condenser E.

In repeating the reasoning just above, one will say that through the valve 8 one can draw out a lighting petroleum (kerosene) well reboiled, still well purified of benzine, but of a little lower boiling point than the kerosene drawn out in 9. Likewise in 7 one will draw out a kerosene still a little lighter and more volatile that that of No. 8.

The zone of the plates C'' is a zone in which is fractionated a product intermediate the benzines properly so called and kerosene, a product known in commerce under the name of, "White spirit"; it replaces essence of turpentine in ordinary colors. The white spirit has been held back from passage by the effect of the third internal condenser F; but the condensed liquid was not homogeneous, whereas after having been reboiled on the plates C'' it is well purified of Benzines which it had held.

In the last place the vapors which have resisted the three condensers D, E and F rise in the plates C''' and arrive at the exterior condenser G and at the cooler H where all are definitely liquified.

The most volatile benzine of all is gathered in *h* at the exit of the cooler H and from there it descends to the test glass No. 1. It has generally a density included between 0.640 and 0.650. It flows to the test glass No. 1 the admission tap of which is regulated in such a fashion as to let only the actual proportion pass which the crude petroleum contains. The excess of it which flows in *h* is forced to pass by the overflow *h'* which brings about the return to the hot reflux from the condenser G.

The mass of these two refluxes arrives on the upper plate [fol. 1025] of the column, and, however serving as a liquid wash for the ascending vapors, it finds its composition modified. The most volatile parts are returned to the vapor,

while the remaining liquid, freed of benzine of 0.650, forms a new quality of benzine a little less volatile and of a density of 0.680 or thereabouts. A part of this benzine is taken off through the tap 2, and from there the liquid, which is boiling, is cooled in the cooler K and goes to a gauge glass No. 2 where the delivery is regulated to a suitable rate.

Every two plates on performs the continuous deductions of liquid of the plates C'''. One can, naturally, either still further multiply these deductions or space them to advantage. The plate column is a real, "Bolting room of essences," and to each taking there corresponds a worm, then a gauge glass No. 3-4-5, where one regulates the volume of each extraction.

The classification of the essences is produced according to the principles already set forth, that is to say, that the reflux liquid of the condenser undergoes a transformation on each plate: volatilization of the lightest elements, and in exchange condensation of less volatile elements. On the other hand it must not be forgotten that, even in the zones C'' and C', there exist in the ascending vapors some extremely volatile elements and one might fear that they would not come to condense in the liquid of plates of these zones, which would stand in the way of fractionation. But theory and experience are in accord to show that there is nothing in that.

The most volatile essences in the vapors pass through the liquids of the plates without stopping and as if these liquids did not exist; it is only the heavy vapors that are retained.

In such manner that the essences extracted in the liquid state in 2, 3, 4 and 5 are very homogeneous, that is to say that in analyzing them in the laboratory one ascertains that between the temperatures of ebullition from the commencement to the end there is but scarcely 10 to 15° deviation for each one.

The respective densities, if one rectifies American crude petroleum will be about the following at the successive gauge glasses:

Gauge glass	No. 1		0.640-0.650
" "	No. 2	About	0.680
" "	No. 3	"	0.700
" "	No. 4	"	0.720
" "	No. 5	"	0.740

[fol. 1026] These products, well classified, find distinct uses in commerce.

The white spirit (gauge glass No. 6) weighs about 0.769. Further down are the burning oils.

Nos. 7 and 8, respectively of about 0.780 and 0.800 density, are petroles de luxe. No. 9 is a more common petrol it still contains a litle heavy oil.

The petroleums have an extremely small specific and latent heat of vaporization so that the radiation from the walls of the apparatus has a great influence. This radiation suffices, in the zone C‴, to eliminate the excess of heat disengaged from one plate to the other. Thus the thermometer T_3 registers about 70° and the thermometer T_4 registers about 140°, that is to say about 70° is lost in seven plates or 10° per plate. This drop works entirely naturally, and besides it must not be forgotten that the proportion of essences in the crude petroleum is not important: otherwise stated the ebullition is relatively moderate in the higher plates.

But it is not the same for the zones C, C′ and C″; there the ebullition is stronger, the digressions of temperature larger, and to be able to conduct the fractionations well is is important to have at its disposition a certain artificial cooling, of a little intensity.

The three condensers D, E, F are constituted of plates with multiple cylindrical chimneys. On the plate and around the chimneys circulates the cooling liquid, so that the vapors condense partially in contact with the bottoms of the plates and the internal walls of the chimneys.

The remainder requires to employ an appropriate cooling liquid but one will well understand immediately that this liquid can not be water.

Condenser F.—The cooling liquid is all simply the reflux itself of the plates C‴, after one has lowered the temperature of it of a suitable quantity in a cooler L outside the apparatus.

The reflux of the plate immediately above F leaves by the tubulature 1, enters the tubular chamber of L, leaves in 1_1, and before re-entering on the plate F, its temperature is established by the thermometer T_7. The re-cooling of reflux L is obtained by an appropriate circulation of water. One can at will carry off 30-50 or 70° from the reflux to accentuate more and more the condensing strength of F, and

to thus oppose a more and more effective barrier to the as-
[fol. 1027] cent of heavy vapors. The refrigerant L can be constructed of a worm if one prefers.

Condensers D and E.—One can use the same system, but it will, however, have a disadvantage. The temperatures of the reflux in these zones here, must be extremely high, so that the water would be almost immediately placed in ebullition in the exterior coolers. Also it is better to use just simply the crude petroleum to be rectified as the condensing liquid.

This crude petroleum, descending from the feeding vessel M, will be regulated by the sensitive valve R, and will enter the condenser E. It there takes a temperature of about 140-150° and will there experience a certain little ebullition, which will drive out the most volatile essences, which will rise freely towards the essence zone C'''. After having passed through the plate E the crude petroleum, already pretty hot will leave by the siphon tube 10-11 to rejoin the condenser D. There it will conclude its heating to beyond 200°, will lose the last essences (white spirit) and leaving again by the tubes 12-13 will finish by entering the heater A.

On the other hand it is not necessary that the reflux come to mix with the crude petroleum, because one will not have more liquid on the plates of C' and of C, and one will not have to withdraw burning oil for the portions 7, 8, 9, it is necessary therefore to lead off the refluxes. For the condenser E this external circuit is made by the siphon tubing 14-15. For the condenser D, it is made by the siphon tubing 16-17.

For the condensation F, one can yet make a full plate which will require the total amount of vapors to pass in the condenser L then re-enter after cooling in the upper plate; but such a condenser would be scarcely regulable because, the water boils at 100° and that the vapors of essences at this stage are above 150°. One would be obliged to place more water than one would want.

Cooling of the withdrawals.—The essences of 2, 3 and 4 go, by three worms separately contained in the reservoir K, to cool completely before flowing respectively to their gauge glasses 2, 3 and 4. The cooler K is fed in abundance by very cold water; at its departure this water is heated only a little. One can send it in the bottom of the lower reservoir N which contains the worms of 5 and 6. Finally

the water leaving N goes in turn into the vessel P which contains the three coolers of the previous deductions 7, 8 and 9.

All of these deductions, after cooling, go to respective gauge glasses which carry the same numbers. At their en- [fol. 1028] try into the gauge glasses, all of the liquids are regulated minutely as to timed withdrawals according to the usages in processes of continuous rectification. The various dial thermometers T_1, T_2, T_3, T_4, T_5, T_6 placed on the stages of the column of plates show at every instant the temperature of rectification of successive plates, and they show to the operator the probable densities which correspond to them. These densities are controlled by the densimeters placed in the gauge glasses, and the skill of the still operator consists in maintaining in each gauge glass a density as constant as possible, in making the withdrawal vary in accordance with the indications of the thermometers.

The streams of various kinds of essences are rather small; one can easily make five categories of essences, as said above, and it is rare that the total represents more than 25% of the volume of crude petroleum placed in rectification.

Whereas when one considers the stage of lighting oils, which is fractioned into three portions No. 7, No. 8 and No. 9, one obtains quite ordinarily 40% of flow and even more. The three gauge glasses 7, 8 and 9 must then suffice for a withdrawal substantially greater than those of the first gauge glasses. One can make them of a much stronger model.

Chemical purification.—The means universally employed for destroying the sulphuretted odors of petroleums consists in treating them with concentrated sulphuric acid. This purification is discontinuous; one charges into the apparatus the petroleum to be purified with a charge of about 2% of concentrated sulphuric acid. One injects into the acid, which is at the bottom of a cylindro-conical receptacle, a strong current of compressed air, which projects the sulphuric acid in every direction, multiplying its contact with the product to be purified.

One treats essences in the same manner but with one condition, that they contain a strong majority of heavier

essences (0.720 and 0.740 density); and yet even in these conditions, one experiences a loss sufficiently serious in the category of the lightest essences.

It is only after the threshing with the acid that one makes the final rectification of the essences.

But with the continuous apparatus which comes to be described, one obtains from the first stroke of the portioning a very good share of essences. If one wishes to thresh with acid the essences of header No. 1 and No. 2, the air will evaporate everything; nothing will remain, indeed, it would [fol. 1029] be fortunate if one did not provoke an explosion through spontaneous combustion at contact with the air. The purifier would be transformed into an immense motor carbureter of air.

It is necessary to obviate this situation, because without that, one will reduce to the immediate fractionation described above.

Figure 1 represents, at the lower part and to the right, a battery of purifiers built on a new principle and solving the problem.

There are as many distinct purifiers as there are categories of essences, consequently five.

Each purifier is composed of two cylindro-conical vessels of sheet iron covered with lead, of very unequal capacity. Each two are filled with debris of small pieces of broken glass. The large cylindro-conical vessel is deluged with sulphuric acid up to about 50 centimeters of its upper edge. As to the smaller vessel, it is filled with water up to about 40 centimeters of *of* upper edge.

The essence from gauge glass 1 descends directly into the lower point of the purifier U_1, and thanks to its great lightness (density three times less than that of sulphuric acid) it rises with great speed to the surface. But the smashed glass divides and subdivides to infinity the globules of essence and of acid. Thus the essence is perfectly desulphurized when it arrives at the upper part of U_1.

But it can retain a little entrained acid. The washer X_1 does not contain acid but water according to needs sharpened with caustic soda. The desulphurized essence leaves by U_1, arrives in the lower point of X_1, rises through the turns of the broken glass, and perfectly washed by the large contact with the water. It leaves definitely in X_1 and goes to be diverted into its particular reservoir V_1.

The same for the four other categories of essences which are purified in U_2, X_2, U_3 X_3, U_4, X_4, U_5, and X_5.

The vessels have the shape of truncated cones because this form assures a better, uniform, division of essence in the acid. But one can make them cylinderical or paralle-pipedic with the condition of putting a double bottom and under this double bottom some distributer tubes of lead pierced with fine holes.

It is to be remarked that the chemical purification may thus be continuous, even as the fractionating column C; it will be necessary, however, to stop the apparatus from time to time to take out the used acid and to replace it with new [fol. 1080] acid. It will be well to have the vessels U_1, U_2 possess a stock of acid calculated in a manner to insure the chemical purification for three or four weeks. One can give variable capacities to the vases, but, even if they are made identical, it will suffice, for each operation, to *to* put in each one only the respective charge of acid which should suffice for it for an identical period.

When the acid is exhausted, one causes it to flow out from the bottom because it is charged with sulpho-compounds.

Placing in operation and management of the apparatus.—One will start by charging the boiler with crude petroleum absolutely as though there had — no change. One will heat gently, as at other times, to drive out the lightest essences and to reach a temperature beyond 100°, that is to say, the temperature of dehydration, which is always to be watched during this period, the takings 5-6, 7-8 will be closed: the apparatus will produce only essences.

When one has arrived at about 105° in the boiler B, one will begin the continuous feeding of the boiler with crude petroleum and in such a manner as to maintain a constant level, that is to say to replace the empty space produced by the evaporation. At the same time one will push the firing. Little by little, the temperature in the boiler increasing, it will occur to practice the withdrawal from the outlet No. 5, then successively from 6, 7, 8 and 9.

During this time the heavy products accumulate in the boiler; the withdrawals of lighting and heavy oils will increase at the base of the column, until it will be necessary to diminish a little the outflow from the gauge glasses 1, 2, 3, 4. There are thermometers which indicate the proportions

to be extracted to always maintain the temperature approximately constant at the various stages of the column.

One will thus arrive at the time when it will be necessary to practice a continuous egress conforming to the heavy products contained in the boiler and from this time on the apparatus will be in an invariable and permanent order of operation and will operate continuously.

But it is, however, to be said that by this mode of operation one can not push very far the exhaustion of the residues in distillable products. It is with difficulty that one can maintain the boiler at 270-280°.

If one wishes to let absolutely nothing but a vaselineous product boiling at 350° at least pass out, the operation can not remain completely continuous; it will be necessary at [fol. 1031] long intervals to cause a liquidation of the boiler, so much the more as at the final temperatures some cracking is produced with the deposition of retort carbon on the walls.

At the end of the 15 or 20 days, according to the capacity of the boiler, it will be necessary to determine to withdraw from the boiler the concentrated tar, to start anew.

Conducted in this manner, the operation is not, properly speaking, continuous, but quasi-continuous, in the sense that the periodicity of the operations is extremely long, and that during these long periods, everything passes as though the apparatus were continuous; in effect, it possesses the characteristics of continuity, continuous feeding of crude petroleum, and continuity of simultaneous and multiple fractionation.

But one can with profit render the operation strictly continuous, and so much the more easily as there will always be a sufficient number of large boilers of the old type in the industry, which the new installation will render available and which can go to complete the continuous apparatus in the following manner:

One will take two boilers with their respective condensers; in each of them one will place two or three transverse diaphragms, with a sufficient orifice at the low point of each diaphragm, in such a manner that the liquid progresses only methodically from one end to the other of the boiler (See figure 2, plan view).

In the continuous apparatus one will be content to extract one half or two thirds of the lighting petroleum contained in the crude, and one will cause a continuous outflow of residuum from the boiler which one will direct to the front of the boiler A_2. At the rear of this boiler A_2 the tubes 18-19 will cause the residual petroleum to pass to the rear of a third boiler A_3, and in this third boiler, the liquid will return towards the front and will leave continuously by the tube 20 and the cooler Z.

One will maintain, with a naked fire, a suitable boiling in the two boilers. The remainder of the lighting petroleum will distil in A_2 accompanied by a certain quantity of heavier petroleum oils.

In A_3 the density will be very high, the boiling temperature will reach 350°, and cracking will occur to an important extent whereas this can not be said to occur in A_2.

Whoever speaks of cracking speaks of the production of retort carbon; it is then indeed necessary, at a predeter- [fol. 1032] mined moment to empty the boiler to remove this carbon. But that can be done without stopping the continuous operation. In effect, the boiler A_2 will continue to absorb the heavy liquid coming from the continuous apparatus, on condition that one makes a little stronger fire to distil more energetically, and thus make a little more room, the continuous departure of 1819 being momentarily closed. At need, one will permit a certain proportion of the excess of liquid residuum to leave. During this time one will empty and clean the boiler A_3, and when it is again ready, it is to it that one will send the residue from the continuous apparatus whereas A_2 will become the end boiler. One will feed A_3 at the front and the residue will pass through 19-18 into the boiler A_2. And so forth.

By this artifice, the continuous apparatus will never stop. It will no longer be quasi-continuous with very long periods, but actually continuous, which is much more desirable for the perfect fractionation of the light components. Only the two boilers A_2 and A_3 will be periodic with long periods, and that without any inconvenience. The very dense viscous residue will be sent to the black pots.

The new combinations are applicable to all kinds of crude petroleums, whatever may be the relative proportions of essences, lighting oils or of extra-heavy residue.

When the continuous distillation of oil tars is concerned, the apparatus ought to be modified a little, as is represented in figure 3.

In effect, although the principles remain the same, it is necessary to take account of this, that for 100 kilograms of crude material to be distilled, the proportions of volatile substances to be extracted are much less than for crude petroleums. It will be inconvenient, being given a small volume of benzine vapors, to cause the entire quantity of tar to pass into the two interior tubular boilers D and E (fig. 1) because that would constitute too great a cooling for these vapors.

Besides, one knows that the tar contains always a very appreciable proportion of water, and that, in so far as this water is not eliminated, boiling can cause dangerous joltings and impulses.

These two disadvantages will be done away with by placing before the boiler A and the rectifying column C C′ a preliminary apparatus for heating the tar and dehydrating it.

The tar is raised to the upper stage by a chain pump P and diverted, thanks to a funnel tube E to the bottom of the vessel M. In this vessel, the tar goes to begin to become luke [fol. 1033] warm in order to become more fluid. This warming is produced by the worm Q in which circulates and condenses the light benzols and the water vapor disengages in the preliminary apparatus NN′. The mixture of benzol and water runs out through the Gauge glass 5.

The luke warm tar descends to the feed valve R and enters the upper compartment N of the preliminary column.

The column is rectangular, of sheet iron, and is composed of three or four large divisions, whose stock corresponds to one hour's stay of tar for each division. Tubes of live steam *n* permit the heating to be done. One sees finally, except in the upper division, a certain number of vertical tubes *p*, set in the bottom of the division, which serve as chimneys for the free passage of vapors produced in the lower divisions.

The upper division will be heated to between 95° and 100°, that is to say a little below the boiling temperature of water, in order to destroy the emulsion of this water in the tar but without boiling it, therefore without jolting. At the same time there is a light disengagement of the lightest benzines. The water rises to the surface of the tar and evaporates

gently. The outlet tube 6 permits the tar to descend to the lower division.

In the second division, one will heat a little more strongly, towards 110°-115°, and finally in the base, one will reach 135° to 140°. In these conditions, the dehydration is very gradual and without danger; it is complete before the tar enters the boiler A and this is essential in order to avoid explosions.

Once the tar, dehydrated and freed of benzine has entered the boiler, the operation resembles entirely that of crude petrol-um. One forces the fire under the continuous boiler only in such a manner as to extract the middle oils, the naphthaline and the carbolic oils (phenols). The heaviest products (anthracine oils) are left for the subsequent discontinuous boilers.

The various elements of the rectifying column carry the same-letters as in figure 1.

In *h*, at the outlet of the cooler H, one will receive some light benzines which have been able to escape the action of the preliminary apparatus NN'. These benzines go to the gauge glass 1.

The withdrawal of the warmed product 2 furnishes middle oils, comprised between 120° and 180. They are cooled in K and flow to the gauge glass 2.

[fol. 1034] One can, if one wishes, make a supplemental extraction towards 170°-180° in 3.

A little lower down occurs the cooling of the reflux, as in figure 1. Here this cooling is charged with stopping the ascension of naphthaline vapors, which boil at about 216°. It is necessary to take special precautions because the napthaline congeals at about 75-76°. Also one must not feed the cooler L except with hot water leaving the condenser G. Although this water attains 80°, it conserves sufficiently cooling power relative to the reflux which exceeds 180°.

The naphthaline is withdrawn in Q and there also there is necessary a special artifice to prevent the naphthaline from congealing, in order to be able to measure the withdrawal that is made.

For this object, figure has represented a gauge glass particularly for the circulation of hot water.

The gauge glass is composed of a cylinder of annealed glass A, pressed by four little triangles threaded between two settings of bronze with an inset of rubber. The lower

setting form a pedestal and it possesses two branchings *a* and *b* one prolonging the other. The branching *a* curves vertically, and nozzle *a'* which terminates is seen to emerge into the gauge glass.

The curbs of *a* and of *b* each receive a sensitive graduated tap *c* and *d*.

c is designed for the continuous departure of the naphthaline and *d* for a continuous entry of hot water.

The upper setting is of the same model as the lower except that the pedestal is replaced by a little boss on which is fixed a thermometer *t*. The branching *f* does not receive a tap valve, but simply a return tube for hot water. The branching *g* carries a valve *k* which, on the other side is screwed onto the column C.

Finally on the discharge tube *h* is placed a tubulature which connects with the valve *c* and the tube descends in a reservoir B.

Here is how one causes this assembly to operate; before beginning the withdrawal of the naphthaline by the valve *k*, one introduces hot water through *d*. This hot water can be taken from the cooler L, fig. 3. The water is permitted to circulate for some time, it overflows through *fh* and goes to reheat the bottom of the reservoir B. The valve *k* can then be opened, and as the naphthaline is denser than the water, the size of the jet of naphthaline which descends to the lower [fol. 1035] part of A is seen very well. The naphthaline is permitted to take a certain level and the valve *c* is regulated in such a manner as to maintain the level constant. The naphthaline leaves through *c* and *d* descends in the vessel B in company with the hot water which prevents congealing.

In the vessel B, separation in two superposed layers, the level of which are seen through the glasses D. The naphthaline is withdrawn into pails to let is congeal and to carry it to the refinery. The excess of hot water leaves through the tube F.

The gauge glass A permits of gauging the flow of the naphthaline. It suffices to gauge in advance the glass globe, and to place an arrow at the base to serve as zero and another near the top to indicate five liters. One opens *c* sufficiently to cause the naphthaline to flow out, and cause its level to reach the zero mark. At this moment, one consults a *watch* stop watch and closes *c* entirely. One waits until the level reaches the five liters mark and notes the

time again. One can thus calculate the timed withdrawal according to the number of seconds which has been required to withdraw five liters.

This special gauge glass can be used with advantage for very light essences of petroleum, in order to avoid their contact with the air, that is to say, their evaporation. In place of hot water one will use very fresh water and as the densities are inverted, one will cause the essence to enter through *a* and to leave through *g*, while the fresh water will enter through *f* and will leave only through *b*.

If one will now look back to figure 2, one will observe that, as figure 1, the column carries a certain number of thermometers, which permit the various withdrawals to be made in such proportions that the temperatures of successive stages do not vary.

At the naphthaline stage one should maintain a temperature of about 215° to 220°.

At the base of the column, the temperature ought to reach about 240°-250° and the withdrawal valves 4 and 5 furnish carbolic or phenolic oils.

These are simply received in receptacles exposed to the air in order that they become cool for the final chemical treatment.

The tar which has entered at the rear of the boiler progresses little by little towards the front. The shifting transversally of the boiler causes the tar to advance only methodically in proportion as it is exhausted in volatile products.

[fol. 1036] When it leaves the front of the boiler, if one wishes to still extract the anthracene oils, one will employ three boilers special discontinuous boilers: one will be filling, the second in distillation and the third emptying to drain the exhausted dry pitch. The three boilers will function in turn and will have nothing special except that the boilers in place of being fed with crude tar receive only a tar already freed of all the products volatile up to about 250°. The condensation is done simply by the air.

Claim

Considered separately the apparatus described are truly continuous and function without any stoppage if one does not require of them that they push very far the exhaustion

either of crude petroleum into lighting oils or of tar oils into heavy oils. Their continuous fractions are perfect, although they have only in all a single heating and but a single rectifying column.

The single column is characteried by the use of internal condensers separating the single column into well determined zones. These zones resemble the successive divisions of a special bolting room inasmuch as from each division one withdraws a liquid of different characteristics and of a definite type.

If one requires that the apparatus push the exhaustion very far into the heavy oils, without any subsequent auxiliary boiler, it can no longer be truly continuous but only quasi-continuous with very long periods.

On the contrary it can be truly continuous if the exhaustion in heavy oils, with a certain cracking, is entrusted to two or three final auxiliary boilers such as described. The combination of the continuous and the aforesaid auxiliary final boilers constitutes a very special combination, corresponding perfectly to the ordinary needs of the petroleum industry. As to that of the tar oils, the auxiliary apparatus further added before the rectifying column will not be indispensible if the tar is well dehydrated. It will then be reduced to a simple preliminary warmer.

Emile-Augustin Barbet, rue Saint-Honoré, 173, Paris.

[fol. 1037] PETITIONER'S EXHIBIT No. 139

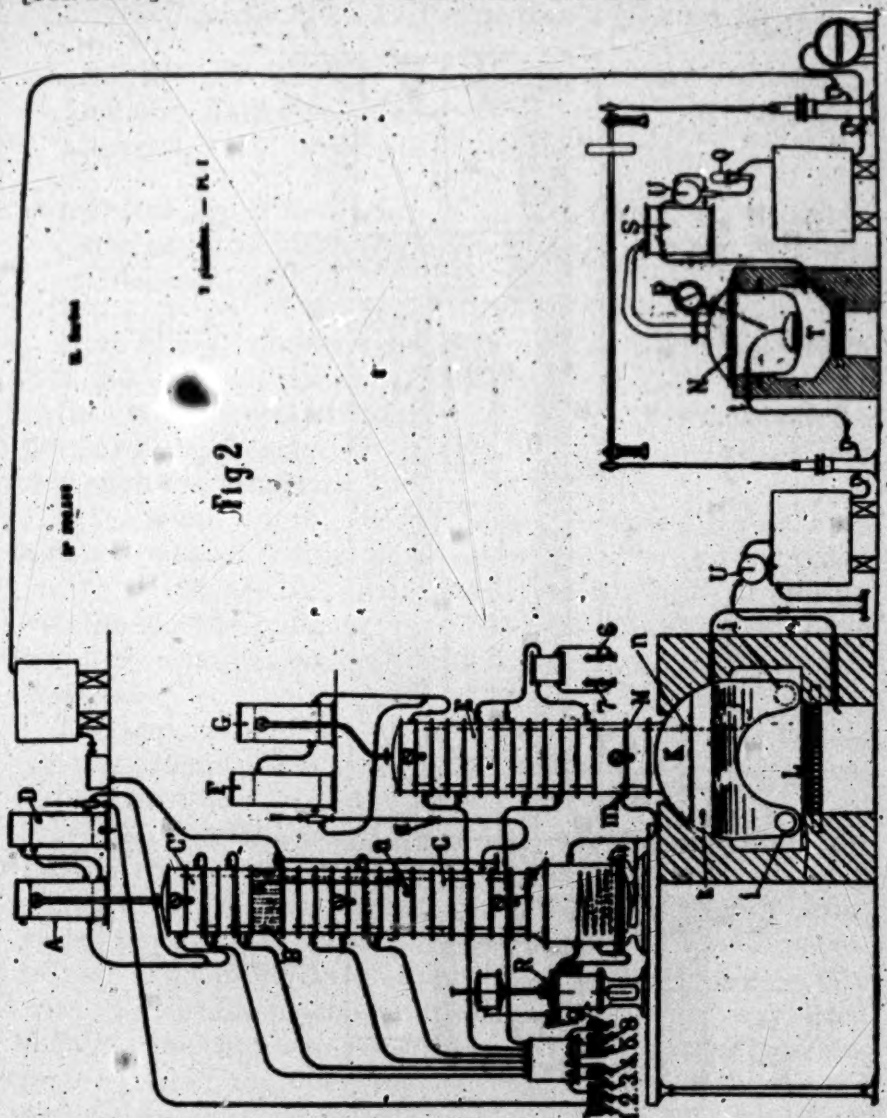


Fig 2

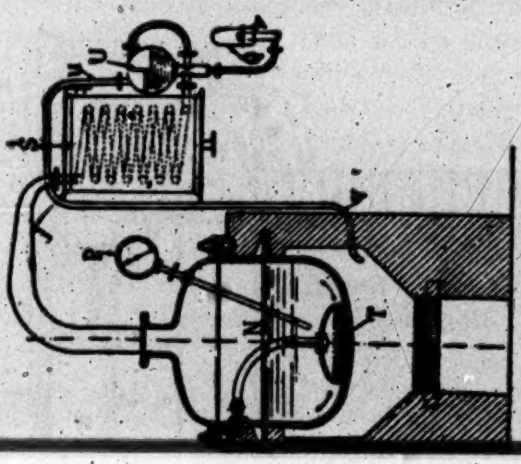


Fig 1

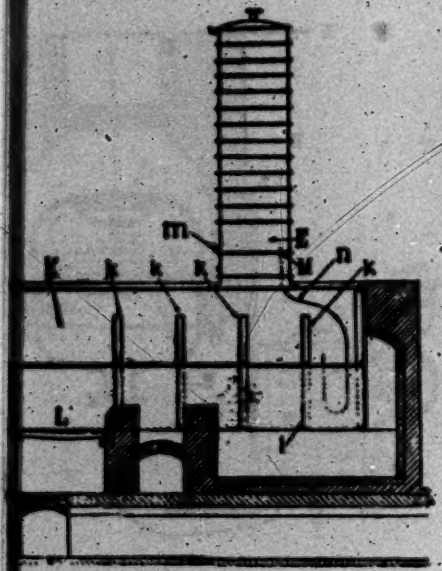


Fig 3

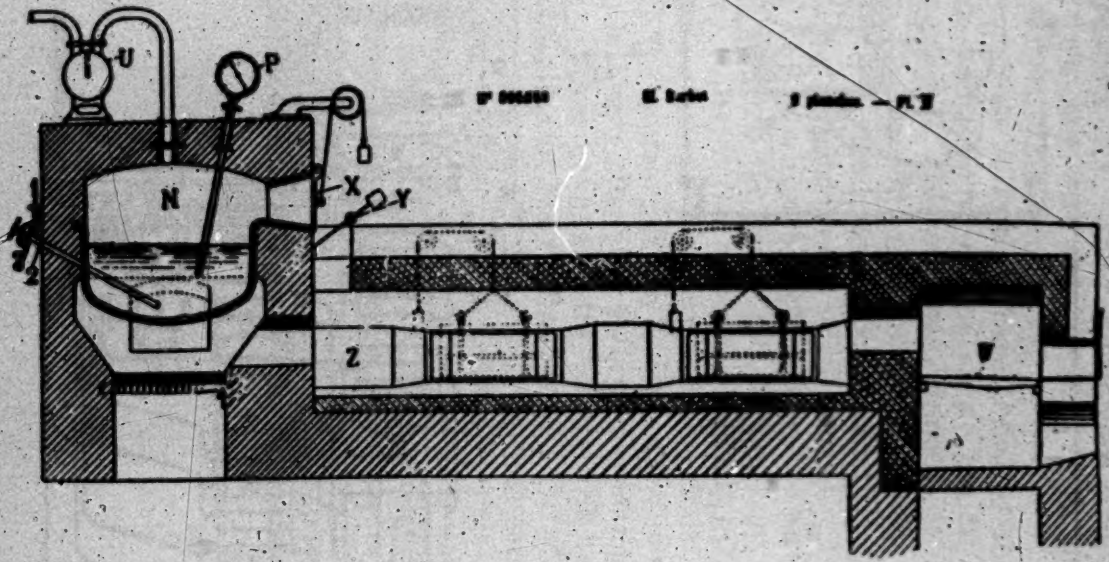


Fig 4

[fol. 1039] TRANSLATION OF PETITIONER'S EXHIBIT No. 139

Translation of French Patent No. 390,558, to Emile-Augustin Barbet. Applied for July 31, 1907. Granted August 1, 1908. Published October 9, 1908

Apparatus for Dissociation of Liquid Industrial Residues Combined with a Continuous Rectification of the Products of Dissociation

Most liquid industrial residues such as heavy petroleum oils, gas or wood tars, turpentine, vinasse, molasses, are of little value in comparison to the products which can be obtained by thermal distillation causing a more or less thorough dissociation.

If the temperature of dissociation is extremely high, only gas is produced (manufacture of oil gas); but there is generally advantage in going much further and producing volatile liquids and not gases. These liquids themselves are very complex and generally need to be separated or rectified.

The apparatus which are to be described fill this double purpose, the problem being at first considered for the petroleum industry.

In this special case, it should be noticed that the light liquids which are produced by dissociation of the heavy oils are of the same nature as those that already exist under the name of volatile oils or gasoline in crude petroleums. The products of dissociation will be seen to mix with the crude petroleum to be subsequently subjected together to continuous rectification, in such a way that complete cycle of the operations if composed of three phases and consequently of three successive parts: that which extracts the volatile oils or gasolines; that which separates out the lamp petroleum, finally that which causes dissociation of the residuary heavy oils in producing new proportions of gasoline and lamp oil. Let us suppose that by old processes, or by the particular continouus rectifier described below, a residue of vaseline-like oils has been obtained and that instead of extracting the vaselines there is commercial interest in destroying these vaseline for obtaining from [fol. 1040] them volatile oils and lamp oils. Then recourse is had to either the old system of "black-pots" or the new

decomposing apparatus shown in Fig. 1. It must be remembered that the vaseline-like residue has a boiling point that it generally equal to or *so* exceeds 340 deg. Centigrade.

N is a large retort of cast metal, with cover bolted on. S is the coil, Q the gage. Lead is put into the boiler and melts at a temperature quite close to the temperature of distillation of the oily residue. If the molten lead is heated to 450 or 500 deg. and heavy oil is continuously injected in it, by means of a small pump, each injection will change immediately into vapor, and then this vapor while passing through the lead bath in bubbling will be dissociated. The decomposition will depend upon the temperature of the bath which can be regulated fairly exactly by using a pyrometer P.

T is a cap of cast metal with openings. The heavy oil is admitted through pipe *t* and upon contact with the superheated cast metal changes into vapor. This vapor occupies all the lower part of cap T and escapes in small bubbles through the openings of the cap. There is no portion which can escape dissociation.

The cracking is always accompanied by a depositing of carbon. The carbon in the present case cannot adhere at any spot. As it is very much lighter than the lead, it rises to the surface of the bath and as the latter is in perpetual agitation the carbon cannot agglomerate.

At the end of a certain period of operation, the retort is opened and the floating carbon is removed with great ease; the interruption will be of very short duration.

The lead cannot oxidize since the bath is kept permanently in contact with the forming carbon and at a very high temperature.

This type of decomposing apparatus can likewise act as distilling apparatus for hydrocarbons with very high boiling point, such as vaseline. By regulating the temperature of the lead bath towards 400 deg. the vaseline will be distilled with little decomposition.

On the contrary, if of commercial interest as at present, lamp oil even can be fed to the lead bath at high temperature for dissociating a part and producing volatile oils of more value.

In this case, the plant will be composed of only two phases: the extraction of the volatile oils and the dissociation.

The lead bath offers the great advantage of having an important range of heat, which can be regulated at a fairly [fol. 1041] exact temperature for producing exactly the dissociation which is suitable to the chosen temperatures.

As to gaseous hydrocarbons, they are separated in a cylinder U placed above the gage and from there they are sent through the pipe u, v into the furnace to be burned, thus economizing in fuel.

As means of heating the lead bath, the use of inferior gases from a gas generator is very appropriate on account of the east this will give in regulating the temperature. The burned gases can be then sent under the boiler K of the lamp oil apparatus (Fig. 2).

In other words, the present model of dissociating apparatus is characterized by the use of a heating means—a lead bath—whose temperature is easy to regulate and to maintain, lead bath in which the heavy hydrocarbon is dissociated by bubbling, the lat-er assuring regular contact of all the molecules with the dissociating agent.

The lead bath can be only a function of a distilling apparatus for industrial products whose distilling temperature is higher than that of the fusion of lead. It can likewise be installed in the present petroleum plants instead of the black-pot.

Metal baths with lower melting point can be used—alloys of lead and tin for instance—for special needs.

The apparatus described allows considerable increase in the output of volatile oils from any crude petroleum. The process can be carried to the limit of not producing anything but light fractions; for this it suffices to give the dissociating apparatus sufficiently large proportions and to feed it directly with petroleum with the gasoline removed. The distillate will contain a mixture of lamp oils and volatile oils which will be separated by the apparatus for continuous rectification which is to be described at present.

Apparatus for Extracting Volatile Oils

The apparatus for exracting volatile oils is shown at the left of Fig. 2.

The crude petroleum mixed with products recovered by dissociation is pumped into a vessel placed at the upper part and from there it enters the coil B before entering at

a into the volatile oil extractor C C′ which has the shape of a distilling column with plates.

There are two types of plates: the lower plates C re- [fol. 1042] ceive the crude petroleum to be distilled and to be freed from its volatile oils. The upper plates C′ on the contrary serve for classifying the various volatile liquids according to their boiling points.

The lightest gasolines (0.62 to 0.66 density) rise to condenser A and cooler D and leave by gage No. 1.

From the upper plates *of* C′, the extraction is made in liquid state of gasolines of about 0.700 density. Some plates lower the density about 0.720.

The petroleum heater B, by the partial condensation it produces, serves for preventing the less volatile liquids from rising. From the plates below B, there can be removed, still in liquid state, volatile oils of 730-740 density and still lower 750-770 density.

These five different kinds of volatile liquids extracted at the point designated, flow all the time, each to a gage, at the entrance to, which there is a cock for regulating the flow. All the liquid should not be withdrawn from the plates, for the apparatus would no longer act as an extractor. The respective flow from the five gages should be regulated according to the composition of the crude petroleums to be rectified and the workman in regulating the proportion of this flow takes into account the readings of the various thermometers which have been placed on each of the extraction plates.

If the upper extraction of plates C′ is taken into consideration for instance, the volatile oil extracted which has 700 density boils at an average at 96 deg. If the thermometer goes down to 92 deg., it signifies that not enough gasoline has been drawn off at gage No. 1, and that there remains some of it at this upper plate. If on the contrary the thermometer rises towards 100 deg., it signifies that too much gasoline at 700 is withdrawn and that the following gasolines at 720 begin to encroach upon the upper part.

The workman at the same time has yet another method of control by the various densities at the gages. From these two related indications of temperatures and densities, the flow to be required from the successive gages can be easily

regulated for maintaining good homegeneity of the products.

When the crude petroleum reaches the bottom of plates C it should be freed entirely from all part- boiling below 160 deg. The boiler, then, should possess a source of heat which attains about 180 deg.; it could be obtained in a very normal way with steam generators stamped for 10 kilograms and with good heat insulation. On the drawing, the [fol. 1043] heating is assured by a high pressure steam coil; direct fire might be used but it is more dangerous in the neighborhood of volatile oils and is much less easy to regulate in an exact way for the various classifications of the volatile liquids.

R is a steam regulator. The five volatile oil gages are numbered one to five by order of density of the products, No. 1 being for gasoline.

3rd. Separation of lamp petroleums.—For lamp petroleums, the homogeneity of the products is not as indispensable, and there is no need to make a great number of classifications.

In general two classes only are required:

1. A so-called high grade petroleum, of a density less than 800 and containing no heavy oils.

2. A more common petroleum exceeding 800 in density and in which there is sometimes 15% or more heavy oils whose presence is detrimental to the brill-ancy of the flame.

The apparatus for distilling the lamp oil consists of two parts: the members for vaporizing and those for classifying the distilled products, (Fig. 2).

In commencing with the latter E, they are very like those of the first column for volatile oils. The vapors coming from the vaporizing members rise through the plate column and are condensed in the condenser F and the cooler G. The whole of what is liquified in condenser F descends again on to the upper plates E. As to that liquified and cooled in cooler G, it is divided into two parts; a small portion regulated by cock *g* returns to the volatile oil extractor C C′ because there are still some volatile oils in this product either because the extraction of volatile oils was not complete in C C′ or more likely because new volatile

oils were formed by dissociation in the vaporization members K.

The remainder of the main liquid joins the warm flow from G and re-enters the plates E above. It is this liquid mixture which in descending from plate to plate is freed little by little from its most volatile products as a result of the re-boiling to which it is subjected by the rising vapors. From step to step the composition of the liquid is changed, the density and boiling point rising progressively as the steps are descended.

As in C C′, extractions are made, at various plates, not of petroleum vapors, but of these re-boiled liquids made nearly homogen-ous by this re-boiling. The two upper extractions leading to gages 6 and 8 furnish petroleums at the same time of the quality grade (because heavy oil can- [fol. 1044] not rise to these steps) and of the safety grade (because the re-boiling has expelled the last traces of volatile oil).

The following extraction will give common petroleum mixed with a little heavy oil (gage No. 9). Finally at the ower extraction (gage No. 7) a nearly pure heavy oil can be collected, a heavy oil which the manufacturer can use as desired and in proportion as desired either to be mixed with common lamp oil or for lubricating oils.

As to the vaporization itself of the crude petroleum previously freed from gasoline in C C′ it is carried on either in several successive boilers or in a single boiler K suitably partitioned so that the liquid passes only successively from one compartment to the other and so that it is thoroughly freed from all lamp oil before it reaches the final outlet.

Fig. 3 shows a longitudinal section of boiler K. A series of diaphragms *k* are shown there, each having an opening 1, some to the right and some to the left. For passing an opening in the following one, the petroleum is obliged to pass over the inner dome of the boiler and be subjected to boiling there. It finally arrives above grate L whose radiation expels the last quantities of the lamp oil with a certain proportion of heavy oil. The vapors of all the compartments are joined to rise to the classification plates E.

The flames from gate L pass to the end of the boiler, under its longitudinal dome, and then divide up to return at the sides.

The admission of the petroleum freed from gasoline takes place at *m;* the liquid is boiled on plate M by the bubbling

of the vapors from K, then it returns by the bent back overflow pipe *n* going into the first compartment of the boiler and from there into the following compartments.

It is of course understood that any other form of boiler can be used, or even several boilers entirely separate from each other provided that the vapors emitted unite in the classification column E.

Although the dissociating apparatus was described first it is understood that in reality in the operation of the cycle of the three operations, the extraction of gasolines is first, while the dissociation must of necessity be the last. Actually, it is necessary at the beginning to have a residue of heavy oil to set the dissociating apparatus in operation.

In the combination of the dissociating apparatus with the continuous rectifier, the latter becomes more and more indispensable to the combination when in carrying the dis-[fol. 1045]sociation still further, more and more volatile oils and lamp oils are produced with heavy residues.

The combination can be reduced to the combination of a dissociating apparatus and a volatile oil extractor, if it is desired, in starting from crude petroleum, to produce only volatile liquid in dissociating even the lamp oil.

The lead bath dissociating apparatus can serve for all other residual liquids with very high boiling point, for instance coal tar, already distilled, for decomposing naphthaline and other heavy products and for producing useful gasolines. These gasolines mixed with the first products from the distillation of tars can be rectified in the volatile liquid separator C C′ and then in the second lamp oil apparatus which in the present case will give xylola, xanthola, etc.

For tars from the distillation of wood, a first lead bath can furnish pyroligneous acids. A second dissociating apparatus with lead bath whose temperature will be higher will liberate combustible gases, acetones, etc.

For turpentines, resins which remain after the extraction of the volatile liquid, can be dissociated in the lead bath. They will give new proportions of essences, of turpentine, illuminating gases, etc, and the carbonaceous residue will form a sort of fine black that can be used either for printing inks or for polishes or paints.

If the lead bath is kept at red heat, the resin just as the vaselin-like oils, will furnish only the illuminating gas called "oil gas." The temperature of the lead bath can be regulated absolutely in relation to the product of dissociation

desired, and if necessary the products can be passed through two or three successive lead baths at increasing temperatures. These carefully determined temperatures give a great deal of homogensity or at least regularity of composition to the dissociation products.

The lead bath can likewise serve for distilling and dissociating the organic residues such as concentrated vinasses from molasses distilleries. It is well known that these residues are extremely difficult to distill in a closed vessel because they foam in an unrestrainable manner. All is changed if instead of putting the whole charge of vinasse into a retort, it is sent by pump jets into a lead bath at a temperature such that the vinasse is instantly dissociated (fig. 4). This integral and abrupt distillation will give complex products; acetic acid, acetone, methylic alcohol, cyanides, methylates, ammonia, etc. Finally, combustible gases which will burn on the grate and save coal will be [fol. 1046] produced. The sale residue mixed with carbon will rise to the surface to the lead bath. From time to time port X calked with refractory clay will be opened and all the salts floating on the lead will be extracted. These salts are mixed with a great deal of carbon. The whole can be made to fall on an incinerating bed where the carbon will burn, giving hot gases which will heat the lead baths.

In the case of vinasse, bubbling in the lead by means of a cap with openings can no longer be employed. The sale residue opposes it. The vinasse is fed through a collecting pipe 1 and from there goes through a pipe 2 into the red molten lead. A screwed opening 3 will allow cleaning the pipe from time to time. For one lead bath, there will be three or four pipes on the periphery.

The gaseous products and the vapors leave through pipe 4 and go to cylinder U and then to a condenser and a gage, as in Fig. 1.

All the organic materials are destroyed instantly if the lead is sufficiently read and the potassium salts are only mixed with carbon.

Y is a tipping trap for allowing the crude salt to fall on bed Z where the carbon burns.

W is a grate for incinerating the salt carbon. The flames are directed from there under the boiler with lead bath.

The same model can likewise, in certain countries, serve for burning molasses itself, if desired.

Summary:

The basis of the process is the thesis that at each temperature there is a corresponding special composition of the products of dissociation; therefore for each heavy industrial residue, it is necessary to determine the temperature of dissociation which furnishes the most advantageous liquids for commerce. It is likewise necessary for all the molecules of the heavy residue to be exposed to exactly this chosen temperature and during a time that is constantly the same. This was impossible when a large stock of residue was charged in a black-pot.

On the contrary, the present apparatus has a wide range of great heat, as a result of the mass of molten lead and the temperature of the lead bath can be kept at an exact point at the will of the workman. Finally the liquid to be dissociated enters the furnace, so-to-say drop by drop; the volatilization and the dissociation are instantaneous and it can be ascertained that all the molecules are subjected [fol. 1047] to exactly the same temperature of dissociation, that-is-to-say that of the lead bath. For all the molecules, the duration of contact is identical; thus there cannot be variation in the composition of the vapors which pass to the condenser, and liquids of dissociation can be obtained which have the greatest commercial value with minimum loss.

Finally, as a result of the very great density of the lead, there are no longer incrustations of "retort carbon," the surface of the heat passage is always clean, the carbon floats and can be removed with ease.

The plant is of very general use; it can be applied to petroleum industries, to oil tars and to wood tars, to heavy oils of benzene, to turpentines, to resins or even to vinasses of distilling and to molasses from sugar making.

According to the raw material, the carbonaceous residue can be used either for combustion, for making inks or black paints, or finally for the extraction of salts. The small amount of gas, the formation of which cannot be avoided, is immediately burned under the lead bath for saving fuel.

Finally, for the liquids whose distillation temperature is very high, the lead bath mixed or not with tin, will be an excellent distilling apparatus because none of the molecules will be subjected to an excessive temperature. In this case, the lead bath, instead of being a dissociating means, on the contrary protects the product against dissociation.

Tr. MMJ.
8/20/25.

[fol. 1048] PETITIONER'S EXHIBIT 140

No. 27,005. (Coat of Arms.) A. D. 1911

(Under International Convention)

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Complete Specification

Improvements in Apparatus for the Continuous Distillation and Purification of Crude Petroleum, Coal Tar, and the Like

I, Emile Augustin Barbet, of No. 173, rue Saint-Honoré, Paris, France, Engineer, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:

This invention relates to the continuous rectification of the fractional distillations of crude petroleum and of coal tar.

In apparatus for this purpose, as heretofore devised, the vapours from the products in the still or boiler heated by direct fire, ascend two or three separate and successive columns containing the usual plates. This apparatus is, moreover, very complicated, and it is the object of the present invention to provide simplified apparatus for the above purpose.

With this object in view, the present invention consists in apparatus comprising a single rectifying column, provided with a still or boiler heated by direct fire, and con- [fol. 1049] taining the usual plates and caps, the column being divided into a number of zones by the interposition of internal tubular condensers, for the purpose of effecting

such a degree of partial condensation of the ascending vapours that the condensate descends through the plates of the column and is boiled again, so that any light constituents contained therein are evaporated, leaving at each zone, to be subsequently drawn off, in a liquid state, spirits petroleums or oils which are perfectly homogeneous as regards volatility.

It has hitherto been proposed to separate and extract from benzines and other liquids, by fractional distillation, the several liquids having different boiling points, by means of apparatus comprising a single distilling column containing the usual trays and caps, but above the caps of each tray a hood is provided, whereby, when the benzine vapours ascend the column, they undergo successive partial condensation upon the underside of the hoods, the condensed liquids being collected directly by gutters provided one on each hood, and are led away through suitable pipes, the condensing being effected by the downflow of the liquid from one tray to an adjacent one below, in such a manner that the liquid is distributed over the hoods. Should, however, the ascending vapours not be sufficiently cooled, then a portion of the liquid on one trary is cooled in outer chamber by the circulation of cold water the temperature of which is not regulated before being discharged onto the hood of the tray immediately below. This apparatus is of very complicated construction. Moreover it will be observed that in this apparatus the fractional distillates are not rectified and cannot therefore be homogeneous.

The present invention is moreover characterised by the combination of the improved rectifying apparatus with auxiliary boilers for the purpose of obtaining a continuous distillation by carrying on to a very great extent the extraction of heavy oils, and by a particular combination for the distillation of the tars and the extraction of the naphthalene. In the accompanying drawings.

Figure 1 shows diagrammatically in elevation one form of apparatus for carrying out the present invention.

Figure 2 is a plan view showing a device for effecting continuous working.

Figure 3 is a sectional elevation of two of the boilers of the plant illustrated in Figure 2.

[fol. 1050] Figure 4 shows in elevation a modification for the continuous distillation of coal-tar.

Figure 5 is a detail view showing a special test glass for the extraction of the naphthalene.

Figure 6 is a front elevation of the test glass, whilst.

Figure 7 is a vertical sectional elevation of one of the condensers.

As illustrated in Figure 1, the present apparatus comprises a large boiler A heated by naked fire, provided with a dome, which through a pipe B and a valve *b* sends the vapours not directly into a condenser coil but into the base of a rectification column composed of several zones C, C^{1}, C^{11}, C^{111}, of plates provided with caps said zones being separated by condensers D, E, F.

Thermometers T^{1} to T^{v} indicate the temperatures of the various parts of the column.

From cocks 2, 3, 4, 5, 6, 7, 8, and 9 are taken liquids at different parts of the column as indicated hereafter.

The heterogeneous vapours ascend through the lower of cap plates C of the column and arrive first in the condenser D which arrests a part of the less volatile vapours. A condensation is produced that is to say, a liquid falls upon the two or three cap plates of the base of the column. This condensation liquid is thus subjected on the plates of the zone C at the base of the column to a new automatic ebullition which transforms again into vapours the volatile elements, so that if, through the cock 9, the reboiled liquid is drawn off, there is collected a product free from volatile elements, a lighting or rectified petroleum well freed from spirits.

The vapours which have not been condensed by passing through the condenser D pass now through the liquid of the second zone C^{1} of the plates, this liquid being derived from a partial condensation produced in a second internal condenser E.

Through the cock 8 it will be possible to draw off a rectified or lighting petroleum well reboiled and therefore free from spirits, but having a boiling point slightly lower than the petroleum drawn off through the cock 9; also through the cock 7 will be drawn off petroleum still slightly lighter and more volatile than that from the cock 8.

The zone C^{11} of the plates is one which is divided into fractions a product intermediary between the spirits proper and rectified petroleum, this product being known [fol. 1051] in the trade under the name of "white spirit"

and it is a substitute for spirit of turpentine in the common colours. The white spirit has been retained by the action of the third inner condenser F, but the condensed liquid was not homogoneous, whilst after being reboiled on the plates of the zone C^{11} it is completely freed from the light spirits it had retained.

Lastly the vapours which have passed through the three condensers D. E. F. pass upwardly through the plates of the zone C^{111} and arrive in the outer condenser G and in the cooling apparatus H.

The most volatile spirit of all is collected at *h* at the outlet of the cooling apparatus H and from there it passes downwardly to the test glass No. 1 the inlet cock of which is adjusted so as to let out only the real proportion of spirit contained in the non-refined petroleum. This spirit has generally a density comprised between 0.640 and 0.650. The excess of liquid which flows through *h* is forced to pass through the overflow h^1 which sends it back towards the hot retrogradation of the condenser G.

The whole of these two retrogradations arrives on the upper plate of the zone C^{111} of the column and while serving as washing liquid for the ascending vapours, its composition is modified. The most volatile parts are transformed again into vapours, whilst the remaining liquid, freed from spirit having a density of 0.650, forms a new quantity of spirit a little less volatile and having a density of about 0.680. A part of this spirit is taken through the cock 2 and from there the liquid, which is boiling hot passes through the cooling apparatus K where it is cooled, and into the test glass No. 2 where the outflow of said liquid is adjusted to a suitable rate.

From two to two of the plates of the zone C^{111} continuous takings are effected, through the cocks 3, 4, 5, of the liquid of these plates. Of course, these takings can be still more multiplied or they made be made further apart. The plate column C^{111} effects the classification of all the spirits of different volatilities; and to each cock there corresponds a coil and then a test glass (Nos. 3, 4, 5) where the volume of each extraction is regulated.

The classification of the spirits is produced according to the principles already mentioned, that is to say that the retrograded liquid of the condenser undergoes a transformation on each plate; volatilization of the lightest ele-

ments and in return condensation of the less volatile elements. On the other hand it must not be forgotten that [fol. 1052] even in the zones C^{II} and C^{I} there exists in the ascending vapours extremely volatile elements and it might be feared that they may be condensed in the liquid of the plates of these zones, which would be prejudicial to the division into fractions. But theory and experience are in agreement for showing that nothing of this sort happens.

The more volatile spirits, in the form of vapours pass through the liquids of the plates without stopping therein and as if these liquids did not exist; only the heavy vapours are retained.

In this way the spirits extracted in the liquid state at 2, 3, 4, 5, are very homogeneous, that is to say that by analyzing them in the laboratory it will be seen that between the boiling temperatures of the beginning and of the end there is scarcely but 10 to 15° C of difference for each.

The respective densities of non-refined American petroleum when rectified will be about the following at the successive test-glasses:

Test-glass	No. 1	0.640	0.650
"	No. 2	about	0.680
"	No. 3	"	0.700
"	No. 4	"	0.720
"	No. 5	"	7.740

These products well classified are used in commerce for different and distinct purposes.

The white spirit (test glass No. 6) has a density of about 0.760. Lower down are the lighting petroleums.

The liquids collected in the test glasses No. 7 and 8 having respective densities of about 0.780 and 0.800 are petroleums of first quality.

The No. 9 is a petroleum of more ordinary quality because it contains a small quantity of heavy oils.

The petroleums have extremely small specific heat and latent heat of vaporization, so that the radiation of the walls of the apparatus has a great influence. This radiation suffices, in the zone C^{III}, for eliminating the excess of that available from one plate to the other. Thus the thermometer T^{3} indicates about 70° C, and the Thermometer T^{4} indicates about 140° C, that is to say a loss of about

70° C in seven plates or 10° C per plate. This decrease of heat is effected in a very natural way and moreover it must not be forgotten that the proportion of the spirits in non-refined petroleum is not considerable, in other words the ebullition is relatively moderate in these plates of the top of the column.

[fol. 1053] But the same is not true for the zones C, C^{1}, C^{111} where the ebullition is stronger and the differences of temperature greater, and in order to be able to suitably carry on the division into fractions, it is necessary to employ a certain amount of artificial cooling of small intensity.

The three internal condensers D E F are formed of vertical tubes 31 fixed by rolling with a mandrel or by screwing in the lower plate 32. The tubes are free at their upper ends. The tube 33 is slightly lower than the tubes 31 and serves as an overflow.

In the working of the condenser F, the example, the refluxes of the upper plate descend by way of the overflow pipe 34 into a basin, then through the pipe *l* to the cooler L where they are cooled and return through the pipe l^{1}. The petroleum vapour from the lower plates coming in contact with the plate 32 and the tubes 31 experience a partial condensation which collects upon the lower plates. At the same time the refluxes which have entered through l^{1} are heated again and passing through the outlet of the overflow 33 they descend to the lower plate where they mingle with the condensed products coming from the condenser tubes.

It will be noted that the liquid contained in the condenser is free to enter into ebullition; the vapor arising therefrom will mingle with the un-condensed vapour and this mixture will rise to the upper zones.

The condensers D and E are similarly constructed with the exception of the pipe 33 as hereinafter explained, but in these cases it is crude petroleum which serves as the condensing liquid; at the same time this crude petroleum enters into ebullition, and the spirits which are freely given off therefrom rise to the upper zones of the plate column.

In the condenser F the cooling liquid is simply the reflux of the plates of the zone C^{111} after the temperature of said liquid has been lowered to a suitable degree in a cooling device L arranged outside the apparatus.

The reflux from the plate which is just above the condenser F issues through the pipe connection l, enters the tubular chamber of the cooling apparatus L issues again at l^1 and before re-entering in the condenser F its temperature is indicated by the thermometer T'. The cooling of the reflux in the cooling apparatus L is obtained by a suitable circulation of water. 30—50 of 70° C can be removed at will from the reflux, for accentuating more and more the power of condensation of the apparatus F and thus opposing a more and more efficient obstacle to the ascent of the heavy vapours. If it is preferred the cooling apparatus L may be constituted by a coil.

[fol. 1054]

For the condensers D and E the same arrangement might be used, but however, there is an inconvenience. The temperatures of the refluxes in these zones become extremely high, so that the water would be almost immediately raised to boiling point in the outer cooling apparatus. Thus it is preferable to use as condensing liquid the non-refined petroleum to be rectified.

This non-refined petroleum, coming down from the feed tank M, will be controlled by the cock R and will enter the condenser E. It will be raised therein to a temperature of about 140—150° C. and will undergo a slight ebullition which will drive away the most volatile spirits, the latter will then pass freely upward towards the spirit zone C^{111}. When it has passed through the condenser E the non-refined petroleum, already rather hot, will issue through the siphon-pipe 10 for entering the condenser D. There it will be heated to a temperature above 200° C., will lose the last spirits (white spirit) and issuing again through the siphon-pipe 12, 13 will enter the boiler A.

On the other hand the refluxes must not be mixed with the non-refined petroleum, as there would be no more liquid on the plates of the zones C and C^1 and no rectified or lighting petroleum could be drawn off through the cocks 7, 8, 9. It is therefore necessary to turn off the refluxes: for the condenser E this external circuit is effected through the siphon-pipe 14, 15 and for the condenser D through the siphon-pipe 16, 17.

The cooling of the extractions is ensured in the following way.

The spirits supplied by the cocks 2, 3, 4, pass, in order to be completely cooled, through three special coils contained

in the tank K before flowing respectively to their test-glasses 2, 3, and 4. The cooling apparatus K is abundantly fed with very cold water; on issuing from this apparatus the water is only slightly heated. It may be sent into the bottom of the lower tank N which contains the coils corresponding to the cocks 5 and 6. Finally, the water issuing from the tank N passes into the trough P containing the three cooling devices for the takings drawn off through the cocks 7, 8, 9.

All these takings after cooling, pass to the respective test-glasses which all bear the same numbers. On entering the test glasses, all the liquids, are minutely regulated in [fol. 1055] their hourly outflow, according to the methods used in continuous rectification. The various thermometers T^1 to T^6 provided with dials and arranged on the stages of the plate column show at any moment the rectification temperature of the successive plates and they warn the operation of the probable densities corresponding thereto. These densities are ascertained by density meters arranged in the test glasses, and the skill of the operator consists in maintaining in each test glass a density as constant as possible by varying the outflow according to the readings of the themmometers. The outflow of the various kinds of spirits is rather small; five classes of spirits can easily be made as mentioned above and it is quite unusual that the whole represents more than 25% of the non-refined petroleum undergoing rectification.

From the stage of the rectified or lighting petroleum which is fractionated into three takings cocks 7, 8, 9 40% of outflow and even more is pretty often obtained. The three test-glasses Nos. 7, 8, 9, must therefore suffice for an outflow considerably greater than that from the first test-glasses. They can be made of larger size.

The extractions from the several stages are finally discharged into their respective tanks V^1—V^6.

The starting and conduct of the apparatus are effected in the following manner:—

The boiler is charged with non-refined petroleum and is heated slowly, as formerely, to drive off the lightest spirits and to raise the temperature above 100° C., that is to say, the temperature of dehydration that must always be watched. During this period, the cocks 5, 6, 7, 8, are closed and the apparatus produces only spirits.

When a temperature of about 105° C., is reached in the boiler A, the latter is fed continuously with non-refined petroleum and this in order to maintain the level constant, that is to say for replacing the vacuum produced by the evaporation. At the same time the fire is urged. By degrees, the temperature in the boiler increasing, it is necessary to draw off at the cock 5 and then successively at the cocks 6, 7, 8, 9.

During this time the heavy products accumulate in the boiler; the takings of rectified or lighting petroleum and heavy oils increase at the base of the column, whilst the overflow of the test-glasses Nos. 1, 2, 3, 4, must be slightly distinguished. The thermometers indicate the proportions to be extracted for maintaining the temperatures approximately constant at the various stages of the column.

[fol. 1056] Thus the time is reached when it is necessary to effect a suitable continuous outflow of the heavy products contained in the boiler and from that moment the apparatus is in unvariable and pertinent normal working order, and it works continuously.

By this method of working, the extraction of the residues in distillable products cannot be carried on to a large extent, as the boiler cannot be maintained at a temperature above 270—280° C.

If it is absolutely desired to let out only a vaselinous product boiling at least at 350° C. the operation cannot remain entirely continuous; it is necessary at long intervals to effect a discharge of the boiler, the more so as at the final temperature cracking is produced with deposit of retort charcoal on the walls.

At the end of 15 or 20 days, according to the capacity of the boiler, it will be necessary to extract from the later the concentrated "mazout", for starting up again.

Thus conducted the operation is not properly speaking continuous, but nearly continuous, in this sense that the periodicity of the operations is extremely lengthened and that during these long periods everything is effected as if the apparatus was continuous; in fact, said apparatus possesses the characteristics of continuity, that is, continuous feeding of non-refined petroleum and continuity of the simultaneous and multiplied fractionations.

But the operation may be rendered rigorously continuous with profit and this so much the more easily as there

always exists in the works a rather larger number of large boilers of the old type, which the new plant renders available and which will be able to complete the continuous apparatus in the following manner.

Two additional boilers A^2, A^3 are used with their respective coolers. In each of them there are arranged two or three transverse diaphragms x_1, x_2 in boiler A^2 and y_1, y_2 in boiler A^3 (see Figures 2 and 3). These diaphragms are formed of a number of shutters which can be folded back upon one another to enable them to be passed through the manholes t_1, t_2 of the boilers. They are not required to make a tight joint with the inner walls of the boilers. At their upper parts they are cut off along the horizontal line $u\ u$ at about twenty centimetres above the normal level $v\ v$ of the boiling petroleum in the boilers. The diaphragms x_1, x_2, y_1, y_2, are each provided with an aperture z_1, z_2, z_3, z_4, [fol. 1057] respectively the *the* aperatures in the several diaphragms being arranged alternately on the right and left hand in such a manner that the petroleum entering for instance the boiler A^2 is compelled to follow in the two boilers the zig-zag path indicated by the arrows (Figure 2) having to pass only through the apertures z_1, z_2, z_3, z_4, in order to pass from one compartment to the adjacent one.

It will be perceived, however, that although the liquid is compelled to follow a tortuous and slow course in order to reach the outlet of the boiler A^3, there is on the other hand no hindrance to the disengagement of heavy vapours, because the diaphragms do not extend up to the uppermost part of the boilers and they therefore allow the vapours to mingle freely before these pass out through the pipe V_1, V_2, to the cooler V_3.

The spent residue ("mazout") of heavy oils passes out through the pipes W_1, W_2, to the cooling apparatus Z.

In the boiler A^1 of the continuous apparatus it is sufficient to extract one half or two thirds of the rectified petroleum contained in the non-refined petroleum and a continuous outflow of the residue is effected from the boiler, said residue being sent to the front of the boiler A^2. At the rear part of this boiler A^2 the pipe 18, 19 conducts the residual petroleum to the rear of the third boiler A^3 and in this third boiler the liquid comes back towards the front and issues in a continuous way through the pipe W_2 and the cooling apparatus Z.

A suitable ebullition is kept up, by direct heating, in the two boilers. The remainder of the rectified petroleum will distil at A^2 accompanied with a certain quantity of more heavy petroleums.

In the boiler A^3 the density will be very high, the ebullition temperature will reach 350° C. and cracking will be produced to a considerable extent whilst no cracking so to speak will be produced in the boiler A^2.

Cracking entails the production of retort charcoal; it is therefore necessary, at a determined moment, to empty the boiler for extracting this charcoal. But this can be done without stopping the continuous working. In fact, the boiler A^2 continues to absorb the heavy liquid coming from the continuous working apparatus, provided a little hotter fire be made for distilling more energetically and for thus giving a little more room, the issue from the pipe 18, 19 being momentarily closed. If necessary a certain proportion of the excess of residual liquid is let out. During this time the [fol. 1058] boiler A^3 is emptied and cleaned, and as soon as it is again ready the residue of the continuous working apparatus is sent into this boiler, whilst the boiler A^2 becomes the end boiler. The boiler A^3 will be fed by the front part and the residue will pass through the pipe 18, 19 into the boiler A^2 and so on.

By means of this device the continuous working apparatus never stops. Instead of being nearly continuous with very lengthened periods it has become really continuous, which is much more preferable for the perfect fractionation of the light components. Alone, the boilers A^2 and A^3 are periodic with long periods, without any inconvenience. The very dense vaselinous residue will be sent into the "black pots."

The new combinations are applicable to all the kinds of non-refined petroleums, whatever may be the relative proportions of spirits, of rectified petroluem or of extra heavy residue.

When the continuous distillation of coal tar is to be effected, the apparatus must be slightly modified as illustrated in Fig. 3.

In fact, whilst the principles remain the same, it must be taken into account that here for 100 kilogrammes of raw material to be distilled the proportions of volatile substances to be extracted are much less than for the non-re-

fined petroleums. There would be inconvenience, in view of the small volume of the benzene vapours, in causing the whole of the tar to pass into the the two inner tubular heaters D, E, Fig. 1, because this would constitute a too great cooling of these vapours.

Moreover it is well known that tar always contains a very appreciable proportion of water and that so long as this water is not eliminated, the ebullition may cause dangerous upheavals and surgings.

These two inconveniences will be suppressed by arranging in front of the boiler A and of the rectifying column C, C^1, a preliminary apparatus for heating the tar and dehydrating the same.

The tar is sent to the upper stage by a chain pump P and poured, through a funnel pipe E^1, to the bottom of the tank M. In this tank the tar will become tepid, so as to become more fluid. The tepidness is produced by the coil O in which circulate and are condensed the light benzols and water vapour given off by the preliminary apparatus N^1, N^{11}, N^{111}. The mixture of benzol and water flows away through the test-glass No. 5.

[fol. 1059] The tar which has become tepid passes downwardly to the feed cock R and enters the upper compartment N^1 of the preliminary column.

The column is rectangular, made of cast-iron and composed of three or four large casings N^1, N^{11}, N^{111} the volume of which corresponds to about one hour stay of the tar for each casing. Live steam pipes *n* serve to effect the heating. It will be seen that there is arranged, except in the lowermost casing, a certain number of vertical pipes *p* set in the bottom of the casing and acting as chimneys for the free passage of the vapours produced in the lower casings.

The casing N^1 is to be heated between 95 and 100° C., that is to say slightly below the ebullition temperature of water, so as to destroy the emulsion of this water in the tar, but without ebullition of said water and therefore without upheavals. At the same time there is a slight evolution of the lightest benzenes. The water rises to the surface of the tar and slowly evaporates. The outlet pipe 21 allows the tar to pass down into the casing N^{11}.

In the second casing N^{II} the heating will be slightly higher, about 110—115° C. and in the lowermost casing N^{III} a temperature of 135 to 140° C. will be reached. In these conditions, the dehydration is really gradual and without danger; it is complete before the tar enters the boiler A, and this is essential in order to avoid explosions. The boiler A is provided with transverse partitions which are arranged in a similar manner to those of the boilers A^2 and A^3 previously described.

In case the tar is well dehydrated, this auxiliary apparatus is not indispensable and can then be reduced to a simple apparatus for bringing the tar to a tepid state. The fire under the continuous boiler A is so urged as to extract only the middle oils, the naphthalene and the carbolic oils (phenols). The more heavy products (anthracenic oils) are left for subsequent additional boilers.

The various parts of the rectifying column bear the same reference letters as in Figure 1.

At *h* the outlet of the cooling apparatus H the light benzenes that may have escaped the action of the preliminary apparatus N^1, N^2, N^3 will be collected. These benzols pass to the test-glass 1.

The extraction of pasteurised product supplied by the cock 2 give middle oils comprised between 120 and 180° C. They are cooled at K and flow to the test-glass No. 2. [fol. 1060] If desired, a supplementary extraction can be made at about 170—180° C. by the cock 3.

A little lower is the cooling of the refluxes as in Fig. 1. Here this cooling has for its purpose to stop the ascent of the naphthalene vapours, which boil at about 216° C. Special precautions must be taken because the naphthalene coagulates at about 75—76° C. Thus the cooling apparatus L must be fed only with the hot water issuing from the condenser G. Although this water reaches 80° C., it largely keeps sufficient cooling power relatively to the refluxes which exceed 180° C.

The naphthalene will be extracted at Q and there also a special contrivance must be provided for preventing the coagulation of the naphthalene, whilst having the possibility of measuring the extraction that is being made.

For this purpose Figures 5 and 6 show a peculiar test-glass with circulation of hot water.

The test-glass is composed of an annealed glass cylinder A^4 clamped by four small screw threaded rods, not illustrated, between two mountings made of bronze with interposition of rubber. The lower mounting forms a support and is provided with two branches *a* and b^1 in line with the one with the other. The branch *a* is curved vertically and the small nozzle a^1 which terminates the same extends into the test-glass.

The flanges of the branches *a* b^1 each receive graduation cocks *c d*; the cock *c* is intended for the continuous issue of the naphthalene and the cock *d* for the continuous admission of hot water.

The upper mounting is of the same type as the lower mounting, with the exception that the support is replaced by a small base upon which is secured a thermometer *t*. The branch *f* does not receive any cock, but simply a pipe for the discharge of the hot water. The branch *g* carries the cock *k* which on the other side is screwed on the column C.

Finally on the outlet pipe h^2 is arranged a pipe union connected to the cock *c* as illustrated in Figure 6 and the pipe leads down into a tank B^1.

The working of this apparatus illustrated in Figures 5 and 6 is effected as follows:

Before beginning the extraction of naphthalene through the cock *k* hot water is introduced through *d*.

This hot water can be taken from the cooling apparatus L. The water is left to circulate during some time, and it overflows through *f*, h^2 and reheats the bottom of the tank B^1. The cock *k* can then be opened and as the naph- [fol. 1061] thalene in denser than water, the size of the jet of naphthalene which flows down to the lower part of A^4 can clearly be seen. When the naphthalene has reached a certain level, the cock *c* is adjusted so as to maintain a constant level. The naphthalene issues through *c* and passes down in the tank B^1 together with hot water which prevents it from coagulating.

The level of separation of the two superposed layers in the tank B^1 is seen through the glass-plates D^1. The naphthalene is drawn off in pails so as to let it coagulate and for sending it to be refined. The excess of hot water goes out through the pipe F^1.

The test-glass A^4 allows of gauging the outflow of the naphthalene. It suffices to gauge beforehand the glass cylinder and to trace a line at the bottom for indicating zero and another line at the top for indicating five litres. The cock *c* is opened sufficiently for running out the naphthalene and causing its level to correspond with the zero line. At this moment a watch indicating seconds is consulted and the cock *c* is entirely closed. Then the operator waits until the level reaches the line indicating five litres and the time is again noted. Thus it is possible to calculate the hourly outflow according to the number of seconds that has been necessary for extracting five litres.

This special test-glass can be used with advantage for the very light spirits of petroleumn, in order to avoid their contact with the air and consequent evaporation. Instead of hot water very cool water will be used and as the densities are reversed, the spirit will be caused to enter through *a* and to go out through *g* whilst the cool water will enter at *f* and will pass alone through b^1.

The column is provided with a number of the thermometers, so that it is possible to make the various extractions in such proportions that the temperatures of the successive stages do not vary.

At the naphthalene stage a temperature of about 215 to 220° C. will have to be maintained.

At the base of the column the temperature must reach about 240—250° C. and the extraction cocks 4 and 5 supply carbolic or phenolated oils.

The latter are simply received in vessels exposed to the air so that they may be cooled for the subsequent chemical treatments.

The tar, which has entered at the rear of the boiler progresses slowly toward the front. The transverse baffle-[fol. 1062] plates of the boiler compel the tar to advance but gradually in proportion as it is being freed from volatile products.

When it goes out at the front of the boiler, if it is desired to extract the anthracenic oils the boilers hereinbefore described will be used. The three boilers will work successively and nothing special will happen during this time, except that the boilers instead of being fed with non-refined

tar will receive only tar already freed from all the volatile products up to 250° C. The cooling will simply be effected by the air.

To sum up, considered separately, the apparatus described are continuous, that is to say, they work without any stoppage if they are not required to carry on to a very large extent either the exhaustion of non-refined petroleum into rectified petroleum or of coal-tar into heavy oils. Their continuous fractionations are perfect although they possess only a single heating and a single rectification column.

The single column is characterised by the use of internal condensers dividing the column into well determined zones. These zones effect extraction from each casing of a liquid having different characteristics and of a definite type.

If the apparatus is required to carry on to a large extent the exhaustion in heavy oils, without any subsequent auxiliary boiler or boilers, it may no more be really continuous, but only nearly continuous with very lengthened periods.

On the contrary it may be really continuous if the exhaustion in heavy oils, with a certain cracking is effected by two or three final auxiliary boilers such as those described. The whole of the continuous apparatus and of the final boilers forms a very special combination, corresponding perfectly to the ordinary requirements of the petroleum industry. Concerning the coal-tar industry, the auxiliary apparatus placed before the rectification column would not be indispensable if the tar was well dehydrated. It would then be reduced to a preliminary apparatus for cooling the product to a tepid state.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:

1. Apparatus for the continuous rectification of crude petroleums and coal tars comprising a single rectifying column, provided with a boiler or still heated by direct fire, and containing the usual plates and caps, the column being divided into a number of zones by the interposition of internal tubular condensers, for the purpose of effecting such a degree of partial condensation of the ascending

[fol. 1063] vapours that the condensate descends through the plates of the column and is boiled again, so that any light constituents contained therein are evaporated, leaving, at each zone, to be subsequently drawn off, in a liquid state, spirits, petroleums or oils which are perfectly homogeneous as regards volatility.

2. Apparatus as specified in Claim 1, for the continuous rectification of crude petroleums and coal tars, in which the internal condensers comprise essentially a series of vertically arranged tubes secured at their lower ends to a plate extending across the column, the cooling liquid which surrounds the tubes, being either the reflux of the hydrocarbons cooled down to a temperature which can be regulated, or the crude petroleum, which it is desired to rectify, in the latter case there being a free disengagement of the light vapours which mingle with the vapours of the column without hindering the fractionation, the vapours ascending the column having free access to the interior of the tubes of the condenser, whereby a partial condensation is effected thereon and also on the plate to which they are secured, the condensate subsequently falling into the plates beneath the condenser, for the purposes hereinbefore set forth.

3. The combination with apparatus for the continuous rectification of petroleums and coal tars, as claimed in Claim 1, of two other final boilers for the purpose of superheating during a lengthened period the residuary products passing out continually from the boiler of the rectifying apparatus and for obtaining in addition a heavy distillate by decomposing the vaselinous residues, these two auxiliary boilers operating alternately without hindering the continuity of the working of the actual rectifying apparatus.

4. The combination with apparatus for continuous rectification, as claimed in Claim 1, of devices for rendering the apparatus suitable for the continuous and direct rectification of tars, namely a continuous column for the preheating of the crude tar, whereby the latter is deprived of its water of hydration and combined water, before the tar enters the continuous rectifying apparatus specified in Claim 1, and a testing device of special construction for extracting the naphthalene, said testing device having a continuous cir-

culation of hot water in direct contact with the naphthalene, thereby preventing the naphthalene from congealing in the pipes and cocks and in the actual testing device, and yet allowing of measuring the hourly delivery of the naphthalene in the testing device as easily as non-congealable [fol. 1064] oils are measured in other testing devices; the said testing device when working with very cold water being capable of being utilised for measuring the extraction of very light spirits so as to avoid all contact of these spirits with the air and consequently all loss by evaporation, the delivery of the extraction being visible, owing to the non-miscibility of the hydrocarbons with hot or cold water.

5. In apparatus as specified in Claim 4, the provision of a testing device having two pipe connections in its upper part and two pipe connections in its lower part, one of the upper pipe connections and one of the lower pipe connections, serving respectively for the inflow and outflow of the naphthalene, and having each an extension curving vertically inside the testing device, the other two lower and upper pipe connections serving respectively as the inlet and outlet of the hot water circulation, the outlet pipe connection for the hot water and the outlet pipe connection for the naphthalene being connected to a pipe discharging into a tank in such a manner that the naphthalene is discharged in contact with the hot water, whereby the naphthalene is prevented from congealing, substantially as hereinbefore described.

6. The improved distilling and rectifying columns and apparatus, constructed and operating substantially as hereinbefore described and also as illustrated in and by the accompanying drawings.

Dated this 29th day of November, 1911.

Marks & Clerk, 57 and 58, Lincoln's Inn Fields, London, W. C., 13, Temple Street, Birmingham, 25, Market Street, Manchester, and 220 Broadway, New York City, U. S. A., Agents.

Redhill: Printed for His Majesty's Stationery Office, by Love & Malcomson, Ltd.—1913.

A.D. 1911. Dec. 2. N: 27,005.
BARBET'S COMPLETE SPECIFICATION.

Fig.1.

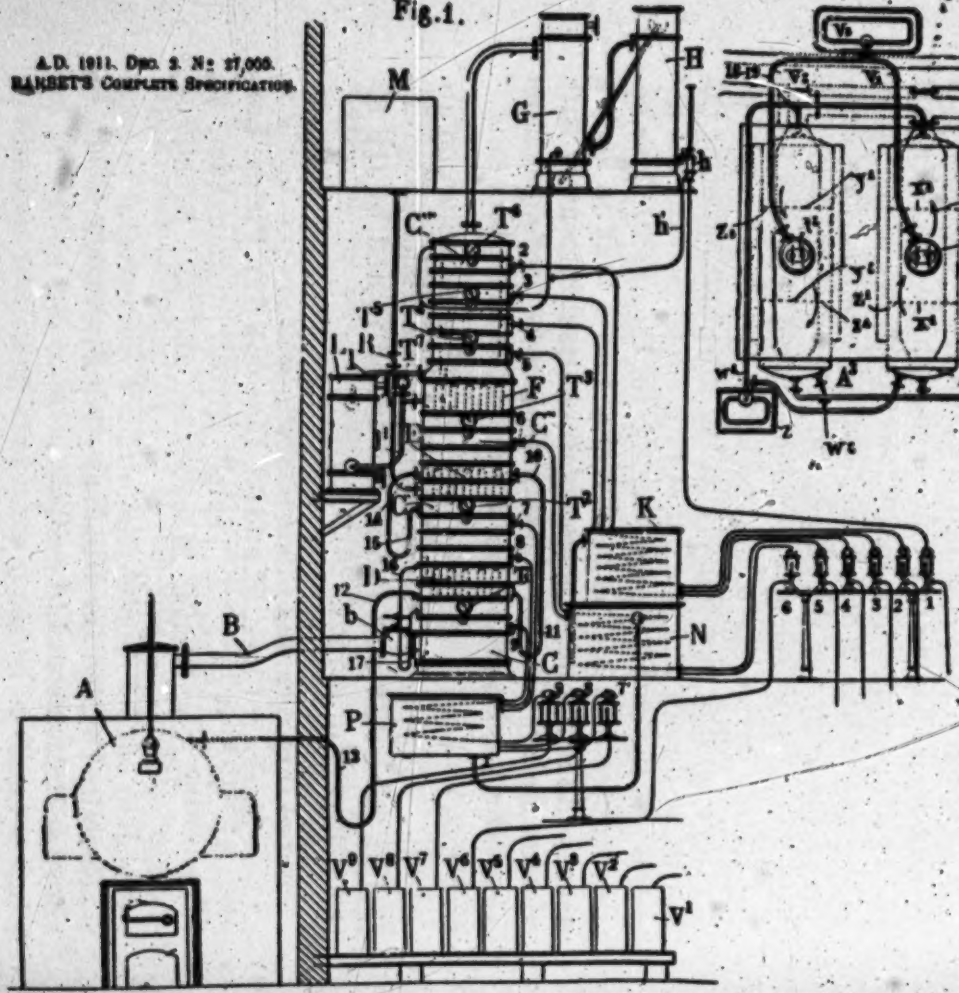
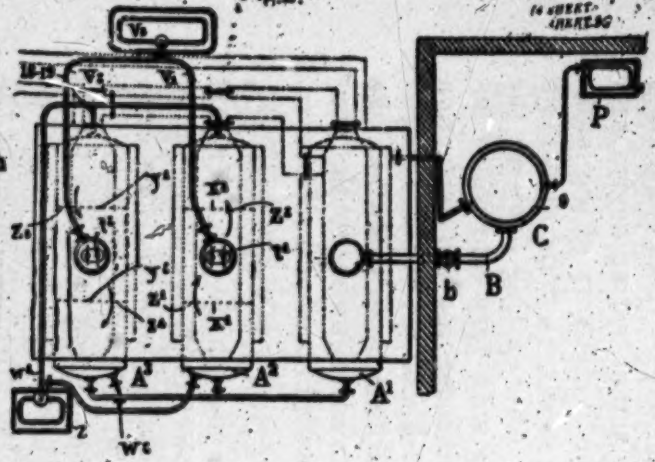


Fig.2.



4328

[fol. 1065]

5106.

4329

A.D. 1911. Dec. 9 N° 27,005.
BARBET'S Complete Specification.

[fol. 1066]

[This Drawing is a reproduction of the Original on reduced scale]

Fig. 6

Fig. 7.

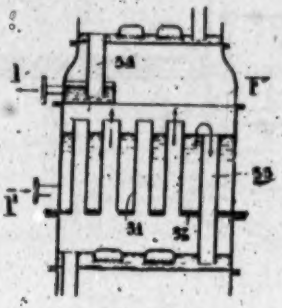


Fig. 3.

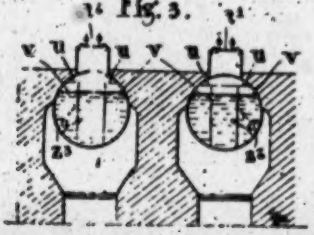
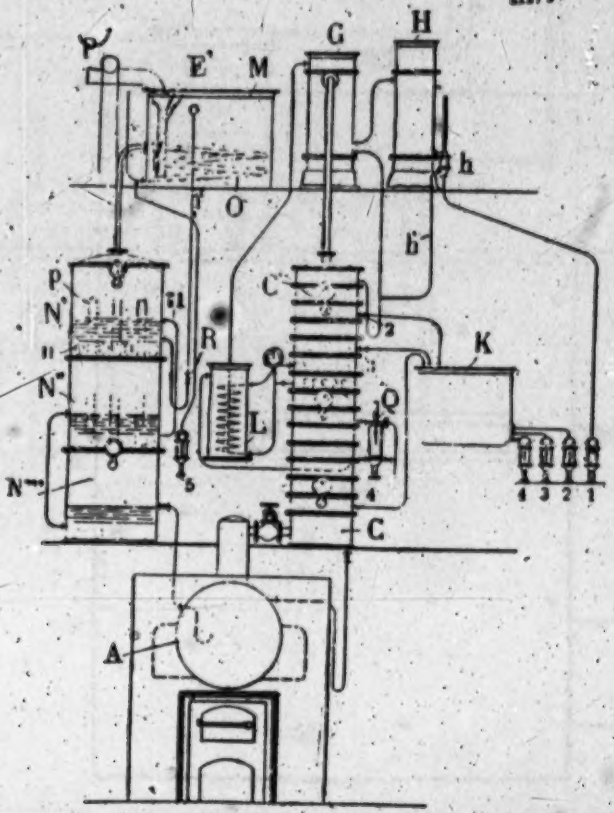


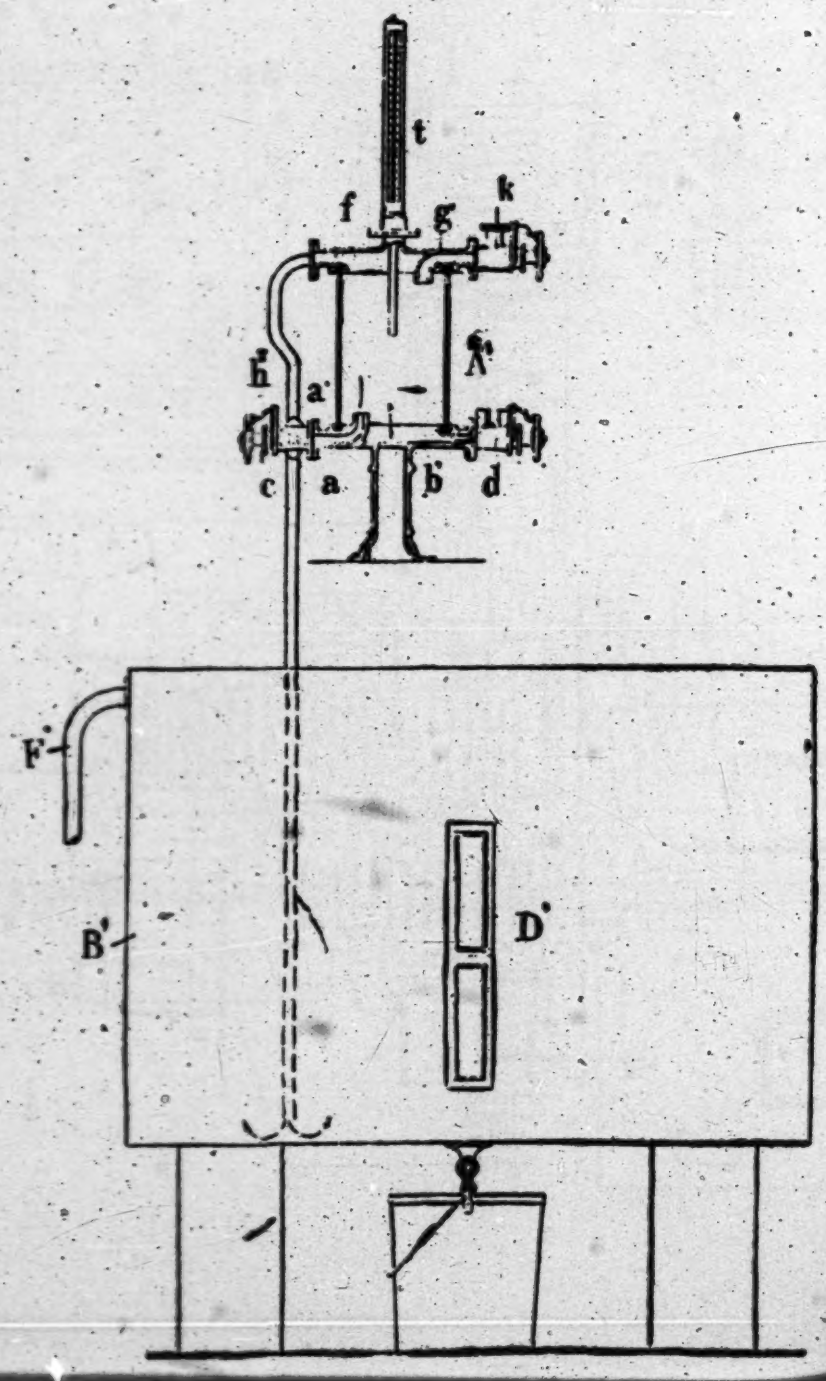
Fig. 4.



[fol. 1067]

A.D. 1911. Dec. 2. N° 27,005.
BARBET'S COMPLETE SPECIFICATION.

Fig. 3.



[This Drawing is a reproduction of the Original on a reduced scale].

[fol. 1068]

PETITIONER'S EXHIBIT 141

No. 836,732. PATENTED NOV. 27, 1906.

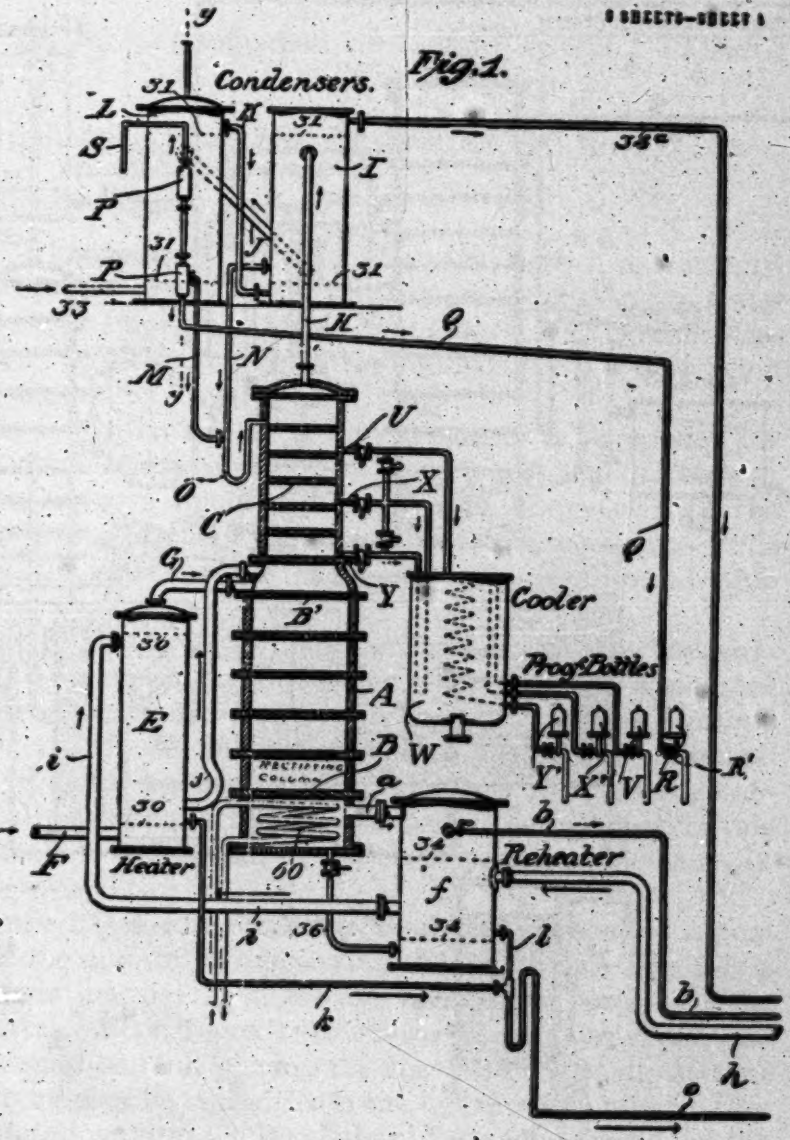
E. A. BARBET.

APPARATUS FOR THE RECTIFICATION OF PETROLEUM.

APPLICATION FILED JUNE 20, 1902.

3 SHEETS—SHEET 1

Fig. 1.



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H. Gilfillan

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Inventor
By Harold Bonney
Atty.

PX 141-1

4332

[fol. 1069]

No. 836,782. PATENTED NOV 27, 1906

E. A. BARBET.

APPARATUS FOR THE RECTIFICATION OF PETROLEUM.

APPLICATION FILED JUNE 20, 1903.

3 SHEETS—SHEET 2

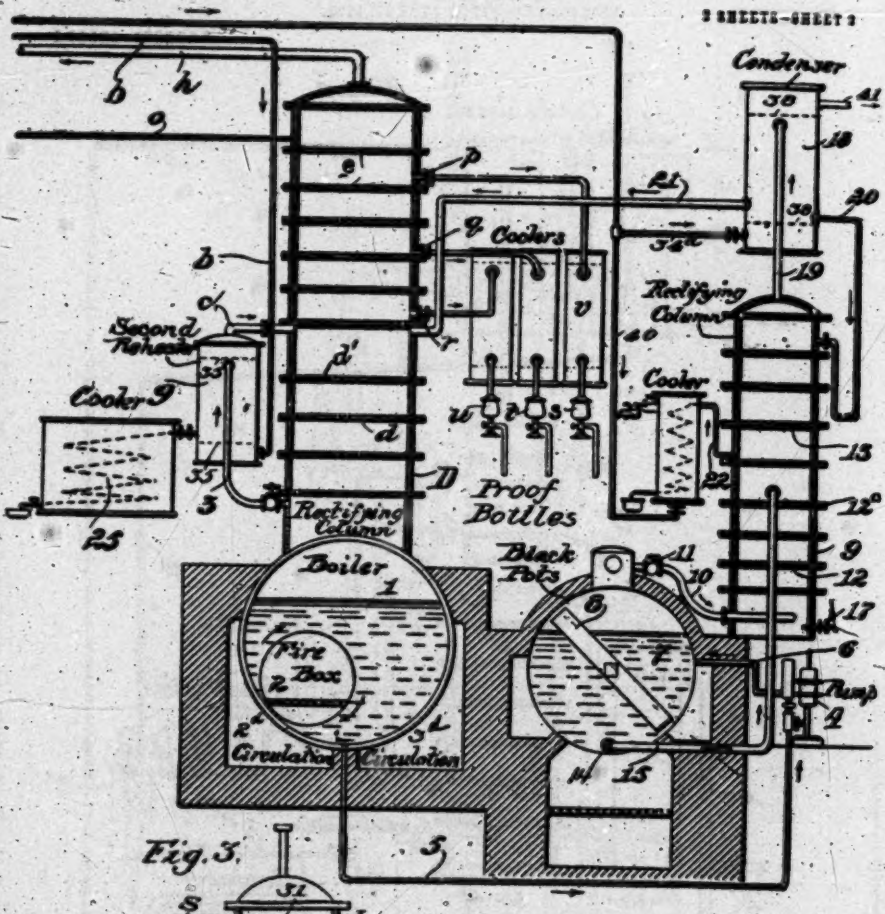

Fig. 3.

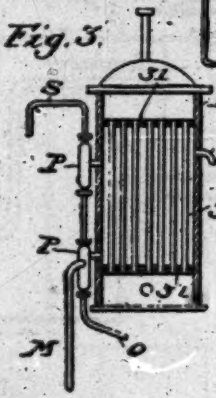

Fig. 2.

Witnesses
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Inventor
by Harold Bunny
Atty

[fol. 1070] United States Patent Office

Emile Augustin Barbet, of Paris, France, Assignor of One-Half to Edm. Jandrier, of Peace Dale, Rhode Island

Apparatus for the Rectification of Petroleum

No. 836,732. Specification of Letters Patent. Patented Nov. 27, 1906

Application Filed June 20, 1902. Serial No. 112,523

To all whom it may concern:

Be it known that I, Emile Augustin Barbet, a citizen of France, residing at Paris, France, have invented certain new and useful Improvements in Apparatus for the Rectification of Petroleum, of which the following is a specification accompanied by drawings.

This invention relates to improvements in apparatus for the continuous rectification of petroleum; and its objects are to improve upon such apparatus, dispense with the costly and unsafe boilers hitherto used, and enable the crude petroleum to be readily separated into its different compounds.

Other objects of the invention will hereinafter appear; and to these ends the invention consists of the apparatus for carrying out the above objects embodying the features of construction, combinations of elements, and arrangement of parts having the general mode of operation substantially as hereinafter fully described and claimed in this specification and shown in the accompanying drawings, in which—

Figure 1 is a side elevation, partly in section, of a portion of the apparatus embodying the invention. Fig. 2 is a side elevation, partly in section, of another portion of the apparatus. Figs. 1 and 2 are shown diagrammatically, and they should be read placing the sheets side by side, so that the piping may be traced from one figure to the other. Fig. 3 is a detail vertical sectional view of the condenser L on the line *y y* of Fig. 1, showing the connection of the piping thereto and the interior construction of the condenser.

Referring to the drawings, A represents a suitable rectifying-column for the oil, provided with perforated plates

B and C. The column A may be heated in any suitable manner, as by means of the steam-coil 60, preferably arranged in the lower portion of the column, which coil may be supplied with steam from any suitable source.

E represents a tubular heater in which the oil to be supplied to the column A is first heated. The heater E comprises a suitable cylindrical casing and tube-sheets in the top and bottom, (represented by the dotted lines 30). The interior of the heater E is constructed like the tubular condenser L. (Shown in detail sectional view in Fig. 3.) The heating fluid circulates around the outside of the tubes of the heater connected between the tube-sheets 30, while the oil passes into the bottom of the heater beneath the lower tube-sheet 30 by means of the pipe F, passes upward through the tubes and out at the top of the heater through the pipe G, which communicates with the rectifying-column A at a point above the upper plate B′ of the lower series of plates B.

I and L represent tubular condensers constructed like Fig. 3, which is a sectional view of condenser L. Each condenser comprises a casing provided with tube-sheet 31, which carry the vertical tubes 32. The cooling liquid enters the lower portion of condenser L by means of the pipe 33, passes up through the tubes 32 into the upper portion of the condenser, then down through the connecting-pipe K to the lower portion of condenser I, thence upward through tubes 32 in said condenser and out by the pipe 34ª.

The upper portion of column A is connected by a vapor-pipe H with the space around the tubes 32 in condenser I, and said space is connected by a pipe J with the space around the tubes in condenser L.

Pipe connections P are provided for condenser L, connected to the space around the condenser-tubes, as illustrated in Fig. 3, and these pipe connections communicate with each other, and from the upper connection P a pipe S extends. From the lower connection P pipes Q and M extend downwardly, pipe Q leading to a proof-bottle R, while pipe M connects with a pipe N, leading from the space around the tubes of condenser I. Pipes M and N terminate in a common pipe O, which leads to the upper portion of the upper part of the column A above the plates C.

According to the construction described the oil entering column A through pipe G passes to the bottom of the column

from plate to plate and is deprived of its most volatile parts. The vapor above the top or feeding plate B′ contains some of the heavier products, which are gotten rid of in the upper portion of the column A and in the condensers I and L. The vapors rising from the top of the column A pass first to the condenser I, where a portion of them are condensed, the lighter products passing through pipe J to the condenser L, where further condensation takes place, and some gases, such as cymogene and rhigolene, escape by [fol. 1071] means of the upper pipe connection P and pipe S to be used in any desired manner. Some of the volatile products condensed in condenser L may pass off through the lower pipe connection through pipe Q to the proof-bottle R, which is provided with a regulating-valve R′. When the regulating-valve is adjusted to only permit a portion of the liquid condensed in condenser L to pass, the remaining portion I term the "excess." All the excess of liquid condensed in condenser L is returned through pipes M and O to the upper portion of the column A, and the vapors condensed in condenser I are returned by pipes N and O to the top of said column. This liquid returning to column A is heated in the upper part of the column on the plate C, whereby most of the volatile parts are volatilized, so that the liquid on said plates is almost entirely freed from its volatile parts, and if from two to four per cent of the liquid is extracted at the point U, for instance, through the piping, as shown, controlled by suitable valves, and through cooler W, a liquid having a low boiling-point and very simple composition will be obtained at the proof-bottle V.

No difference of temperature will be shown from the beginning to the end of the distillation of this product. If some of the liquid is extracted several plates lower down, as at the points X or Y, homogeneous liquids having well-marked differences in specific gravities and boiling-points will be obtained at the proof-bottles X′ or Y′.

It is of course possible to increase the number of products into which the petroleum is separated and obtain liquids having special industrial uses, and these liquids are perfectly clean and transparent, for they have been produced by the condensation of vapors. When the liquid reaches the bottom of column A, it has been entirely deprived of its light constituents, and its composition will

vary according to the composition of the crude oil. It is possible to obtain an oil at the point X having the composition and character of illuminating-oil if sufficient heat is supplied to the apparatus.

D represents another rectifying-column provided with perforated plates *d* and *e*.

f represents what I term a "reheater," because the oil is reheated therein. This reheater *f* in this instance is of tubular form, constructed substantially like the condenser shown in Fig. 3, and is provided with tube-sheets 34, to which the tubes are connected. The upper portion of reheater *f* is connected by pipe *a* with the lower portion of column A. Another pipe *b* connects the upper chamber of the reheater *f* with the lower portion of a second tubular reheater *g*, having tube-sheets 35. (Represented, as in the other instances, by dotted lines.) The upper portion of the second reheater *g* is connected to the column D above the plate *d'* by means of pipe *c*. Suitable means are also provided for circulating the heating liquid around the tubes in the second reheater *g* and also around the tubes between the tube-sheets in the first reheater *f*. As shown, a pipe 3 connects the lower portion of the column D with the space around the tubes in the reheater *g*, and this space is also connected with the coil 25 of a suitable cooler. The top of Column D is connected by means of a pipe *h* with the space around the tubes in the reheater *f*. Said space is connected by another pipe *i* with the space around the tubes in the oil-supply heater E Said space in heater E is connected by one pipe *j* with the column A above plate B', while another pipe *k* connects the space around the tubes in heater E with a pipe *l*, which pipe communicates with the space around the tubes in reheater *f*. The pipes *l* and *k* connect with pipe *o*, which leads back to the top of column D. Another pipe 36, having a valve, connects the lower port of column A with the lower portion of reheater *f*, forming a by-pass.

The purified oil or oil deprived of its light products passes from the lower portion of the column A by means of pipe *a* to the upper portion of reheater *f*, and thence it passes directly by means of the pipe *b* to and through the second reheater *g*, and thence by pipe *c* to the column D. The temperature of the oil is raised in each reheater *f* and

g. The boiling on the different plates of column D causes total vaporization of all the illuminating-oil and even of some of the paraffin-oil, and the separation of these vapors takes place on the plates *e*, as hereinbefore described in connection with the plates C of column A. The vapors from the upper portion of column D may be conducted to a condenser, if desired, but preferably, as shown, these vapors are led by means of pipe *h* to and through reheater *f*, around the tubes therein, and out by pipe *i*, thereby supplying the necessary heat for the reheater. These vapors also supply the heat for the heater E by passing around the tubes in said heater. Some gases may be formed in the oil-heater E, and these escape through the pipe *j* to the column A. If a small excess of the heavier vapors, as illuminating-oil vapors, is not condensed in the heater E, this excess also passes through pipe *j* to column A and there meets the reflux from the plate C. The two refluxes from heater E and reheater *f* return by pipes *k* and *l*, respectively, and the common pipe *o* to the top of column D.

Different grades of illuminating-oil may be extracted from the points *p q r* in the upper portion of column D and led to proof-bottles *s t u* after cooling in the coolers *v*. Suitable thermometers may be used to indicate the operations carried on, and the extraction is regulated in such man- [fol. 1072] ner as to obtain the desired temperatures, which are kept constant.

In this instance a boiler 1 is provided for heating column D. 2 represents the fire-box, preferably arranged eccentrically to the boiler in order to create a circulation. According to this arrangement the left side of the boiler is heated more strongly than the right, because hotter gases forming the second circulation pass through the left-hand flue, and what may be termed the "third" circulation passes through the right-hand flue. Circulation of the liquid thus obtained is in the direction of the arrows in the boiler and prevents the deposit of solid substances and avoids superheating. A small portion of the vapors produced in the boiler 1 may be utilized to heat the reheater *g* by means of the pipe connections described—namely, through pipe 3 and cooler 25. It is advantageous that the purified oil entering column D be as near as possible at the

boiling-point or even be boiling. The boiler 1 should contain a stock of liquid sufficient to regulate the vaporization.

The liquid from the boiler 1 may be pumped into the usual "black pots," but even "cracking," which furnishes more illuminating-oil, may be made continuous. As shown, there is another cylindrical boiler 7, provided in this instance with a stirrer 8, and the exhaust-oil is pumped from boiler 1, through pipe 5, by pump 4, through pipe 6, into the boiler 7. Preferably a pressure of five of six atmospheres is maintained in the boiler 7, and by means of the stirring and this pressure of five or six atmospheres the cracking takes place more rapidly than in the black pots at an ordinary pressure.

9 represents a third rectifying-column connected with the boiler 7 by means of pipe 10. Said pipe is provided with a valve, and, as shown, connection is made with the lower portion of column 9. Said column is also provided with perforated plates 12 and 13.

In the operation of the apparatus the valve 11 is left slightly open in order to permit some of the vapors to be conducted to the bottom of rectifying-column through pipe 10, and at the same time the exhaust-valve 14 in pipe 15, leading to the column above plate 12^a, is left open in order that the liquid may be conducted through pipe 15 to said feeding-plate 12^a. The superheated liquid is partially transformed into vapors, which rise into the upper portion of the column. This formation of vapors produces a cooling, so that the vapors coming from the boiler 7 through pipe 10 are utilized to boil the paraffin-oil in the lower portion of the column, and thus expel all that can be volatilized. The liquid passes out through pipe 17 in the lower portion of column 9, whence it may be conducted to suitable paraffin-presses or to the fire-box to be burned. The separation of the vapors in the upper portion of column 9 takes place as hereinbefore described in connection with the other columns.

8 represents a condenser constructed like the other condensers described with tubes and tube-sheets 38. A pipe 19 connects the upper part of column 9 with the space around the tubes in condenser 18, and said space is also connected by a liquid-return pipe 20 with the upper portion of column 9. Another pipe 21 connects said space around

the tubes with the space above the plate *d'* in column D. The condenser 18 should be fed with hot water, for cold water would solidify some of the paraffin. If necessary, some steam could be introduced in the bottom of the condenser. As shown, the pipe 34ª, leading from condenser I, conducts the condensing liquid to the lower portion of condenser 18, thence through the tubes and out at the outlet 41. The vapors not condensed in condenser 18 pass through the pipe 21 to column D. The paraffin or the oil condensed in 18 returns through pipe 20 to the upper portion of column 9, and having been entirely deprived of illuminating-oil is extracted at the pipe 22 and partially cooled in the condenser 23, which is supplied with condensing fluid by means of the pipe 40, connected to the pipe 34ª. As in the condenser 18, the water in the condenser 23 should be about 70° centigrade in order to avoid the solidification of the paraffin, and the paraffin thus extracted may be afterward bleached and purified.

Some condensation may have occurred in the reheater *g*, and this condensation is cooled in the cooler 25, where care must be taken to avoid solidification of the products. The products of condensation may be sold directly either as vaseline or paraffin or may be returned into the apparatus at the top of the column D.

According to the apparatus described the oil has been separated into ten different lots; but it is of course possible to obtain as many lots as there are plates in the different columns, and the separation may be controlled in accordance with the demands of the trade.

The liquids obtained on the different plates will have a perfectly defined and stable composition, provided that the amount of liquid extracted at the various proof-bottles is just equal in quantity to the feed. A state of equilibrium is thus obtained, provided that the feed is of a constant composition. When this equilibrium is obtained, the separation takes place on the different plates.

The course of the oil in its several fractions is as follows: Oil enters the column A from the heater E, and some of the oil passes to the bottom of the column, while the more volatile parts pass through pipe H to condenser I, whence [fol. 1073] the lighter products pass through pipe J to condenser L, where some gases escape by means of the upper

pipe connection P and pipe S, and some of the volatile products condensed pass off through the lower pipe connection P through pipe Q to the proof-bottle R. The remaining liquid condensed in condenser L is returned through pipes M and O to the upper portion of column A, and the vapors condensed in condenser I are returned by pipes N and O to the top of said column. From the lower portion of column A the oil passes through pipe *a* to the reheater *f* and from thence by pipe *b* to a second reheater *g*, then by pipe C to the column D, and from the top of said column D the vapors pass by pipe *h* back to the first reheater *f*, thence by pipe *i* to the heater E and by pipe *j* back to column A. Some may pass by pipe *k* to pipe *l*, connected to reheater *f*, and from thence a pipe *o* leads back to the column D. From boiler 1 for heating column D the oil is pumped into the boiler 7, through pipes 5 and 6, by pump 4. From boiler 7 the oil passes through pipe 10 to a third column 9 and also through pipe 15 to said column. The liquid passes out through pipe 17 in column 9, and the vapors pass through pipe 19 to condenser 18, and the condensation returns by pipe 20 to column 9. The uncondensed vapors pass from condenser 18 by pipe 21 to column D. Some oil passes by pipe 22 from column 9 to cooler 23.

Obviously some features of this invention may be used without others, and the invention may be embodied in widely-varying forms.

Therefore, without limiting the invention to the construction shown and described nor enumerating equivalents, I claim, and desire to obtain by Letters Patent, the following:

1. In apparatus for the continuous fractional distillation of crude petroleum, the combination of a rectifying-column having a series of upper and lower perforated plates upon which the crude petroleum is partially evaporated, an oil-heater for supplying heated oil to said column at a point between said series of upper and lower plates, means for heating said column, a condenser connected to the upper portion of the column in which the more volatile vapors are condensed, a second condenser connected to the first condenser, connections for leading the condensed products back from both condensers to the upper portion of the col-

umn whereby the vaporization of said products is aided by the heat of the uncondensed vapors rising in the column from the oil distilled on the lower series of plates and means for withdrawing the different products from different points in the height of the column.

2. In apparatus for the continuous fractional distillation of crude petroleum, the combination of a rectifying-column having two series of upper and lower perforated plates, means for heating the column, means for supplying heated oil to said column at a point between the series of plates, a condenser connected to the upper portion of the column, a second condenser connected to the first condenser, connections for leading the condensed products back from both condensers to the upper series of plates in the column, means for withdrawing the products from different points in the column, a reheater connected to the lower portion of said column for raising the temperature of the oil which has been deprived of its lighter products, a second rectifying-column having upper and lower series of plates, a second reheater, connections for leading the heated oil from the first reheater to the second reheater and from thence to a point in the second column between the series of plates, a connection from the top of the second column to the first reheater, a connection for leading the liquids from the first reheater back to the upper series of plates in the second column and means for withdrawing the products from different points in the height of the second column.

3. In apparatus for the continuous fractional distillation of crude petroleum, the combination of a rectifying-column having two series of upper and lower perforated plates, means for heating the column, means for supplying heated oil to said column at a point between the series of plates, condensers connected to the upper portion of the column, connections for leading the condensed products back to the upper series of plates in the column, means for withdrawing the products from different points in the column, a reheater connected to the lower portion of said column for raising the temperature of the oil which has been deprived of its lighter products, a second rectifying-column having upper and lower series of plates, connections for leading the heated oil from the reheater to a point in the second column

between the series of plates, a connection from the top of the second column to the reheater, a connection for leading the liquids from the reheater back to the upper series of plates in the second column and means for withdrawing the products from different points in the height of the second column, a boiler for heating the second column, said boiler having a circulation of oil, a third rectifying-column having upper and lower series of plates, connections for leading the exhaust-oil from the boiler to a point between the series of plates in the third column, a condenser connected to the upper portion of said third column, a connection between the upper portion of the boiler and the lower portion of the third column, connections for leading condensed products from the last-named condenser back to the upper [fol. 1074] portion of the third column, a connection between said last-named condenser and the second column and means for withdrawing the products from the third column.

4. In apparatus for the continuous fractional rectification of crude petroleum, the combination of a rectifying-column having a series of upper and lower perforated plates, an oil-heater for supplying heated oil to said column at a point between said series of upper and lower plates, means for heating said column, a condenser connected to the upper portion of the column, connections for leading the condensed products back to the upper portion of the column, means for withdrawing the different products from different points in the height of the column, a first reheater connected to the first column, a second rectifying-column having upper and lower series of plates, a second reheater, connections for leading the heated oil from the first to the second reheater and from thence to a point in the second column between the series of plates, a connection from the top of the second column to the first reheater, a connection from said reheater to the oil-heater for the first column, connections for leading liquids from the said oil-heater and from the first reheater back to the upper series of plates in the second column and means for withdrawing the products from different points in the height of the second column.

5. In apparatus for the continuous fractional distillation of crude petroleum, the combination of a rectifying-column

having two series of upper and lower perforated plates, means for heating the column, means for supplying heated oil to said column at a point between the series of plates, condensers connected to the upper portion of the column, connections for leading the condensed products back to the upper series of plates in the column, means for withdrawing the products from different points in the column, a reheater connected to the lower portion of said column for raising the temperature of the oil which has been deprived of its lighter products, a second rectifying-column having upper and lower series of plates, connections for leading the heated oil from the reheater to a point in the second column between the series of plates, a connection from the top of the second column to the reheater, a connection for leading the liquids from the reheater back to the upper series of plates in the second column and means for withdrawing the products from different points in the height of the second column, a boiler for heating the second column, said first boiler having a circulation of oil, a second boiler under a pressure of about five or six atmospheres connected to the first boiler, a third rectifying-column having upper and lower series of plates, connections for leading the exhaust-oil from the second boiler to a point between the series of plates in the third column, a condenser connected to the upper portion of said third column, a connection between the upper portion of the second boiler and the lower portion of the third column, connections for leading condensed products from the last-named condenser back to the upper portion of the third column, a connection between said last-named condenser and the second column and means for withdrawing the products from the third column.

Signed this 6th day of June, 1902, at Paris, France.

Emile Augustin Barbet.

Witnesses: Edmond Boniface, Edward P. MacLean.

[fol. 1075]

PETITIONER'S EXHIBIT 142

S. H. EDWARDS.

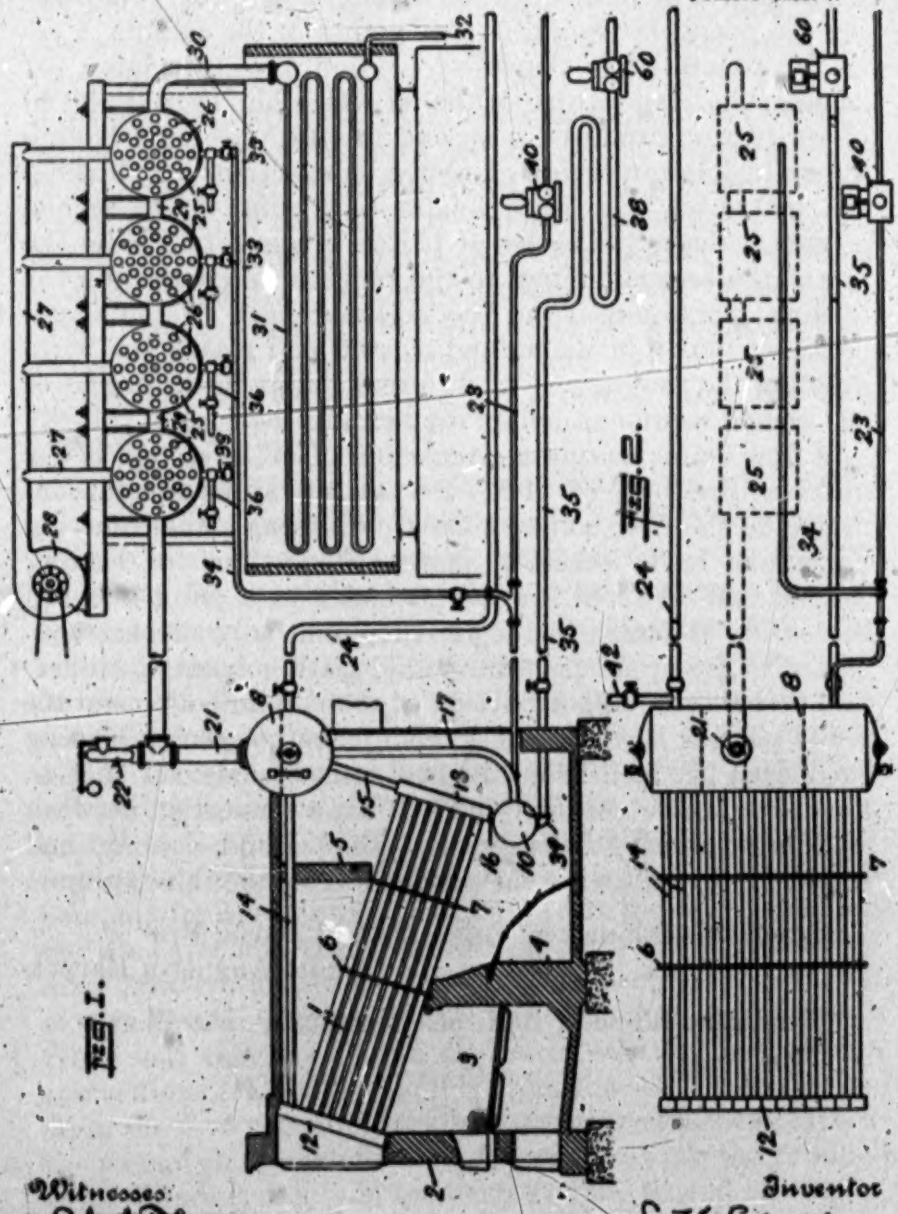
OIL DISTILLING APPARATUS.

APPLICATION FILED MAY 8, 1915.

1,170,884.

Patented Feb. 8, 1916.

3 SHEETS—SHEET 1.



Witnesses:
C. Robert Thomas
E. Greenberger

Inventor
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By his Attorney

PX 142-1

[fol. 1076].

S. H. EDWARDS.

OIL DISTILLING APPARATUS.

APPLICATION FILED MAY 6, 1913.

1,170,884.

Patented Feb. 8, 1916.

3 SHEETS-SHEET 2

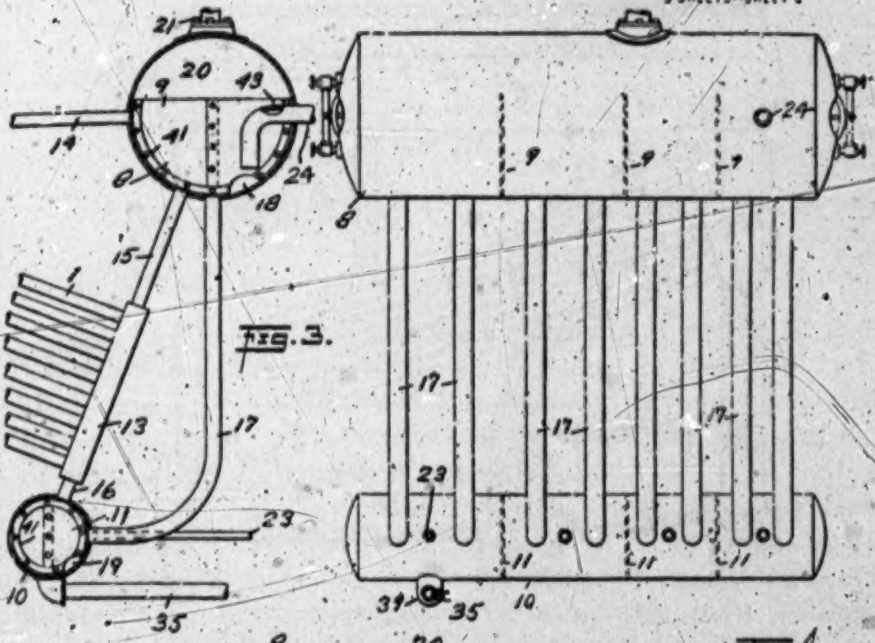

FIG. 3.

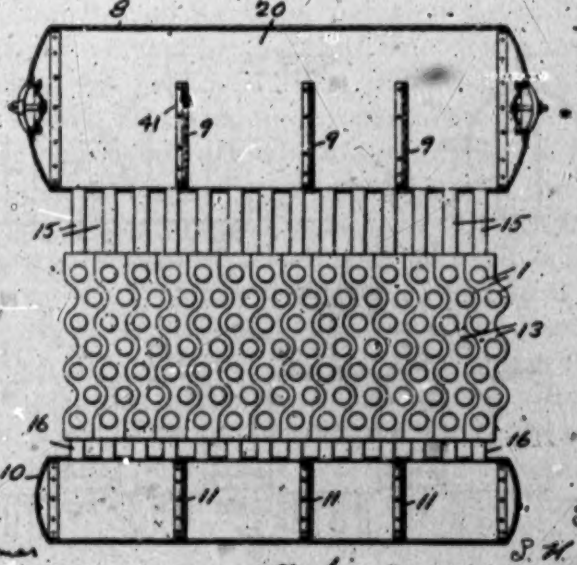

FIG. 4.

FIG. 5.

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Ps 102-2

4346

[fol. 1077]

S. H. EDWARDS.

OIL DISTILLING APPARATUS.

APPLICATION FILED MAY 6, 1915.

1,170,884.

Patented Feb. 8, 1916.

3 SHEETS—SHEET 3

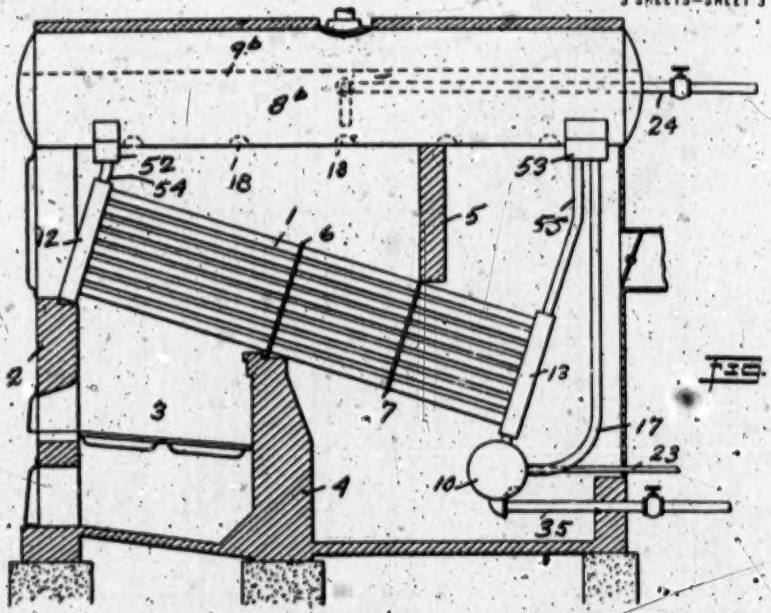


FIG. 6.

FIG. 7.

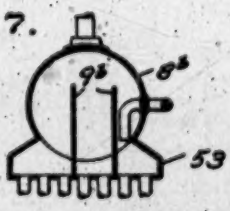


FIG. 8.

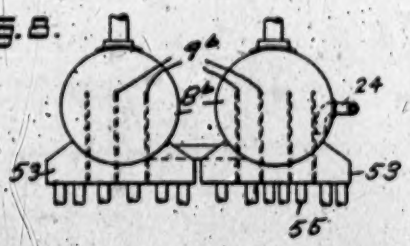
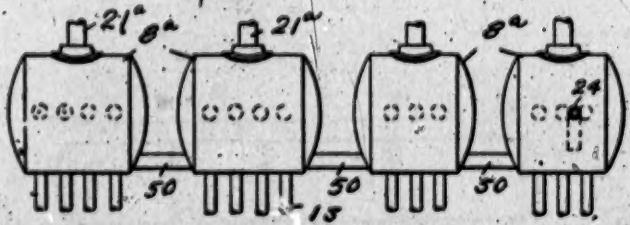


FIG. 9.



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[fol. 1078] United States Patent Office

Samuel H. Edwards, of Bayonne, New Jersey, Assignor of One-Fourth to Tidewater Oil Company, of Bayonne, New Jersey, a Corporation of New Jersey

Oil-Distilling Apparatus

1,170,884. Specification of Letters Patent. Patented Feb. 8, 1916

Application filed May 8, 1915. Serial No. 26,699

To all whom it may concern:

Be it known that I, Samuel H. Edwards, a citizen of the United States, and a resident of Bayonne, in the county of Hudson and State of New Jersey, have invented certain new and useful Improvements in Oil-Distilling Apparatus, of which the following is a specification.

The object of the invention is to provide an advantageous apparatus for the continuous distillation of hydrocarbons.

The apparatus is especially suitable for continuous destructive pressure distillation of relatively high boiling point fractions resulting from petroleum distillation, for the purpose of converting the same wholly or partially into low boiling point products. The invention is not limited in its usefulness, however, to any one process or operation, and may be employed with advantage in place of apparatus used for the distillation of crude petroleum or the redistillation of its distillates in accordance with various procedures.

In the manufacture of gasoline from high boiling point hydrocarbons by pressure distillation, and to a great extent in the art of petroleum distillation it has been the practice to follow the "batch" or intermittent method of distillation, that being made necessary by the type of apparatus employed. This has involved a time loss of perhaps one-third, making only about two-thirds of the actual time employed effective, and compelling the refiner to construct a larger number of units than would have been necessary were it possible to employ the continuous distillation method. Another disadvantage of present day practice is the necessity of building comparatively large reservoirs

or stills in order to start with a sufficient quantity of raw material to make the process economical and practical.

For the purpose of enabling this work to be carried on continuously I have designed a tubular still, composed of drums and heating tubes, sectionalized or partitioned, and so constituted with its connections and supply and discharge lines as to secure an automatic progressive circulation. Among the advantages of the still are cheaper construction and less plant investment than necessary heretofore to process a definite quantity of raw material, a material reduction in operating cost, due to the greater capacity and higher efficiency of the still, obtained by operating continuously, greater safety in operation and practicability of operating at much higher pressure than has been practicable heretofore. The apparatus is particularly suitable for economically and efficiently carrying on pressure distillation to a fractional degree only.

It is well known to those skilled in the art that, within certain limits, the lower boiling point fractions of the oils usually treated by pressure distillation are more easily "cracked," thermolyzed or converted into low boiling point hydrocarbons at the pressures and temperatures usually employed than the higher boiling point fractions of the oil to be treated. My apparatus makes it possible to carry on the process economically and efficiently to a fractional extent only by extending the operation to the degree of having cracked or thermolyzed principally those lower boiling point constituents of the oil being treated which are most easily converted, and leaving as a residue a product suitable for sale and use as a gas oil or fuel oil without further processing. The invention is useful as well, however, for carrying out the distillation of these fractions, or of crude petroleum or other petroleum products, until the residue has been reduced to the degree, desired. In this connection, the still may be made of varying sizes by increasing or decreasing the number of sections, or two or more of the stills may be connected in series, according to the extent to which distillation is to be carried.

Other apparatus may be employed in conjunction with the still, more especially a series of aerial condensers for condensing out of the vapors the fractions of higher boiling points and returning the same to the still or making

other disposition thereof as desired, the several aerial condenser units having individual outlets which may be connected by a common return line with the lower portion of the tubular still at one point, or by separate lines with different sections of the still, or which may be connected with receiving tanks if these fractions are not to be turned back into the still.

Various other features of the invention will become apparent as the specification proceeds.

In the accompanying drawings illustrating the inven-[fol. 1079]-tion: Figure 1 is a sectional side elevation of the apparatus, the pipe lines being shown broken away for economy of space and the stack connected with the furnace of the still being omitted for like reason; Fig. 2 is a plan view of the still and its pipe lines, with the brickwork setting omitted; Fig. 3 is an enlarged vertical longitudinal section through the rear portion of the still; Fig. 4 is a rear elevation of the still; Fig. 5 is a section taken on a plane intersecting the axis of the upper and lower drums of the foregoing figures; Fig. 6 is a sectional side elevation of a modified form of still; Fig. 7 is a cross-section through the longitudinal drum of Fig. 6; Fig. 8 is an end elevation indicating cross-connected longitudinal drums; and Fig. 9 is a rear elevation indicating semi-diagrammatically a transverse arrangement of cross-connected drum compartments.

These views show the preferred form of the apparatus and certain modifications thereof, but it is to be understood that the construction is susceptible of further modification and that changes may be made, and that parts may be added or taken away, as long as the essential character of the apparatus is not altered.

The construction shown in the drawings will now be briefly described. Reference will first be had to Figs. 1 to 5. The still comprises primarily a nest of heating tubes 1, which are shown disposed in a forwardly and upwardly inclined position within a setting 2, the fire-box 3 being beneath the forward, upper ends of the tubes. The course of the gaseous products of combustion from the fire-box is determined by the bridge wall 4, the depending wall 5, and baffles 6, 7 in the nest of tubes, so that the tubes are effectively exposed to the heat. The still also comprises

an upper drum 8, which in accordance with the invention is partitioned by transverse diaphragms 9 so as to present a plurality of compartments which are connected in circuit with groups of tubes. A lower drum 10 is also provided and partitioned by diaphragms 11 like the upper drum, the compartments of the lower drum being connected with the lower or rear ends of the groups of tubes. The still thus consists of a plurality of sections, which may be greater or less in number, each section comprising a group of tubes and therewith connected drum compartments. The still is thus divided into a number of small circulating units, bringing the oil into rapid and repeated contact with the heating surface of the tubes, and allowing the vapor formed in each circulating unit to become disengaged from the liquid in the upper drum. The sections are connected in such manner that while the oil being treated is circulating continuously through the tubes of the various sections and giving up its vaporized portions in the upper drum, a progressive circulation of the oil as residue, less the vaporized portion, takes place from one section to another, successively. As illustrated, the partitions of the upper and lower drums are similarly placed, and corresponding upper and lower compartments are connected with the ends of the same sets of tubes, the communication between sections being through the diaphragms in the drums.

In Figs. 1 to 5, the upper drum is disposed transversely, partly inside and partly outside the rear and upper portion of the setting, above the rear, lower ends of the tubes. The lower drum is placed transversely within the lower rear portion of the setting, and is connected with the rear or lower ends of the tubes. The upper drum is connected with both ends of the tubes. The tubes are connected in tiers with sectional headers 12 and 13, the upper ends of which are connected by tubes 14 and 15 with the upper drum. The lower drum is connected with the lower ends of the headers by short tubes 16. In addition, in order to insure an adequate supply of oil to the heating tubes 1, the lower, or rear, ends thereof are connected with the upper drum by downcomers 17. The latter preferably open into the rear side of the lower drum, and may be two in number for each pair of upper and lower drum compartments, and of the same size as the tubes 15, though this may be varied. The

connections between the drum compartments may be formed by openings 18 and 19 through the diaphragms near but somewhat above the bottoms, in order to guard against their becoming choked by deposits. These openings are preferably comparatively restricted in order that part of the oil in each section may be caused to circulate repeatedly therein before passing to the next section, or, in other words, to render the progress from section to section comparatively slow. Manifestly, however, the action may be varied by making the area of communication for the oil between compartments larger or smaller. The openings also perform the function of equalizing the level of the liquid in the several sections, to guard against any of the sections doing dry.

The diaphragms of the lower drum preferably go all the way to the top thereof, being closed with the exception of the openings 19. The diaphragms of the upper drum, on the contrary, preferably terminate a substantial distance below the top of this drum, so as to leave a common vapor space 20 in the upper part. The same result would obviously be secured by appropriate openings in the upper parts of the diaphragms. From the top of this space there leads a vapor line 21, which may carry a safety valve 22.

[fol. 1080] The supply line 23, for raw oil or distillate to be re-distilled, preferably enters the lower drum, at the compartment at one end thereof. This compartment, the drum compartment above and the connected group of heating tubes constitute the first section. As shown in Fig. 5, the first section may be wider than the last section, including more of the heating tubes. The dimensions of the intermediate sections and the number of tubular units included thereby may vary. The residue discharge line 24 preferably leads from the upper drum compartment of the last section. Its inlet end may be inside the drum, a short distance above the bottom, and may extend upward and thence bend laterally, passing through the wall of the drum at such height that the liquid level determined by the height of overflow is below the tops of the diaphragms, to the end that communication for the oil between compartments shall be confined to the openings 18. A pump 40 in the supply line serves to deliver the fluid to the still at an appropriate rate.

The vapor line conducts the vapors to the first of a series

of aerial condensers 25, which comprise a row of horizontal drums having air tubes 26 passing through them. Air is supplied to these tubes by an air line 27 having a blower 28, the cooling effect being thus definitely controllable. The vapor line enters the side of the first condenser drum, the interior of which around the cooling tubes is filled with the vapors when the still is in operation. The highest boiling point fractions condense here and settle in the bottom of the drum, which thus constitutes its own collector. From the opposite side of the first drum the vapors still uncondensed pass to the second drum by a short tube 29, and so on through the drums in series, fractions of successively lower boiling point being condensed out in the several drums and collecting in the bottoms thereof. The number and size of the aerial condensers may be varied in accordance with conditions and the particular end in view. From the last drum the remaining vapors pass by a line 30 to a water condenser 31, from which the crude gasolene or other distillate may be drawn off from time to time through a line 32. If the operation being conducted is the thermolyzing of high boiling point fractions having boiling points of upward of 400° F. (gas oil, etc.,) for the purpose of producing gasolene, the aerial condensers should be so proportioned as to knock back all of the oil fractions coming over with the vapors having higher boiling points than the desired naphtha-containing distillate, which, alone is condensed in the water condenser.

Each of the aerial condensers has an individual outlet 33 from its bottom, and all these outlets may enter a common return line 34, which joins the supply line 23 and thus reaches the lower drum of the still, preferably entering the first compartment thereof, though this may be varied. In addition each of the aerial condenser outlets has a valved branch 36, and each of the compartments of the lower drum other than the first has a connection 23^a, which may be closed if not in use, so that by suitable piping, the arrangement of which will be obvious, the condensate of any or all of the aerial condensers may be returned to any one or more of the sections of the still, enabling any desired combination to be effected. Or the products condensed in the aerial drums may be drawn off to storage, for other disposition.

A line 35, leading from the bottom of the lower drum, part of which constitutes an extension of the return line, is connected through a cooler 38 with a pump 60, so that in event of emergency the still may be quickly emptied of oil. The drum fitting 39 of the line 35 is preferably located at the bottom of the drum and may be removed to facilitate cleaning out of carbon deposits from this drum. For the same purpose the diaphragms in the drums are made collapsible, so that they may be readily displaced after access is obtained through usual manholes. The particular construction may, of course be varied, but as shown in Fig. 3, the desired end may be simply attained by making each diaphragm in two parts, bolted to each other at the middle and at the margins to angle irons 41 on the interior of the drums.

The overflow line 24, through which the residue escapes from the still may lead to storage, or as indicated by the branch 42 may lead into or constitute the supply line of a second still, which may be in all respects like the first and is therefore not illustrated. While it is possible to build one still with sufficient circulating units to carry on the process to any desired degree of concentration of the residue, it is not advisable for practical reasons to carry the still beyond a certain size, preferably not more than twenty tubes wide, because of mechanical limitations which may be encountered. If it is desired to carry the process beyond the degree of concentration attainable in one such still the liquid residue in the last compartment of the upper transverse drum of the first still may be led to the first section of the lower drum of a second still, and the process carried on from that point in a way entirely similar to that in the first still except that, due to the heavier concentration and the higher average boiling points of the material composing such residue, higher temperatures will naturally prevail. The process may be carried in a third and even a fourth still, to a point where the degree of concentration is [fol. 1081] too great to admit of further practical continuous processing of the residue. At this point the residue will flow out continuously at a rate conforming to the speed of the process and can be collected in a suitable container. A vent opening 43 is formed in the top of the overflow line,

at a point within the drum. The function of this vent is to prevent the possibility of a siphoning action being set up, thereby creating a tendency to lower the level of the oil below the predetermined point fixed by the position of the overflow or discharge line 24. The illustrative modifications of the preferred construction will now be referred to briefly. Fig. 9 shows an embodiment which may be in all essentials like that described, except that the upper drum compartments, 8^a, instead of being formed by partitions in a common drum, constitute separate sections which are cross-connected as indicated at 50. Each of these compartments may have its own vapor outlet 21^a.

In Figs. 6 and 7 a longitudinal drum 8^b is shown, which is divided into partitions by longitudinal diaphragms 9^b, having the same functions as the diaphragms 9. This drum connects with the headers of the heating tubes by boxes 52 and 53, into which the diaphragms extend, and tubes 54 and 55. Otherwise than the longitudinal position of the drum, the still and its mode of operation may be precisely like those of the preferred form, and the construction is so illustrated. Another modification, indicated in Fig. 8, may be exactly like Fig. 6, except that it comprises a number of cross-connected longitudinal drums, located, it will be understood, in the same setting.

What I claim as new is:

1. A continuous tubular oil still comprising a plurality of connected sections comprising groups of heating tubes and therewith connected drum compartments, and means for supplying and discharging oil to and from different sections whereby the oil being heated in circulation progresses from one section to another successively.

2. A continuous tubular oil still comprising a furnace and setting, in combination with a plurality of transversely connected still sections comprising drum compartments and heating tubes connected therewith and exposed to the heat of the furnace, and means for supplying and discharging oil to and from different sections whereby the oil being heated in circulation progresses from one section to another transversely of the still.

3. A continuous tubular oil still comprising a nest of inclined heating tubes, a fire-box under the upper portion

thereof, a plurality of drum compartments above and connected with the tubes, the compartments and therewith connected tubes constituting sections through which the oil circulates successively, a supply line connected with the first section, and an overflow line connected with the last section.

4. A continuous tubular oil still comprising a fire-box, a nest of tubes arranged in the path of the gases flowing from the fire-box, a plurality of upper drum compartments connected in circuit with the tubes, a plurality of lower drum compartments, the drum compartments and therewith connected tubes constituting sections through which the oil circulates successively, and oil inlet and outlet lines connected with different sections.

5. A continuous tubular oil still comprising a furnace, a nest of tubes therein, a plurality of drum compartments, each compartment being connected with the opposite ends of a set of the tubes, whereby the oil may circulate repeatedly in each section comprising a drum compartment and its connected tubes, connections between the compartments whereby the oil may pass from one section to another, and an inlet and an outlet for oil connected with different sections.

6. A continuous tubular oil still comprising a furnace, a nest of tubes arranged in the path of the products of combustion, a drum above and connected with the tubes, diaphragms in the drum dividing the same into compartments, and means whereby the oil being heated in circulation progresses from one compartment to another.

7. A continuous tubular oil still comprising a plurality of connected sections comprising a drum divided into compartments and heating tubes connected with the compartments, and means for supplying and discharging oil to and from different sections.

8. A continuous tubular oil still comprising a nest of tubes, a drum above and connected in a circulatory system with the tubes, diaphragms in the drum dividing the same into oil compartments with a common vapor space in the upper portion of the drum, means for leading off and condensing the vapors from said space, and oil inlet and out-

let lines connected so that the circulating oil passes from one drum compartment to another.

9. A continuous tubular oil still comprising a nest of heating tubes, upper and lower drums connected therewith, said drums being divided into compartments, a supply line, and an outlet for the residue.

10. A continuous tubular oil still comprising a nest of tubes, upper and lower drums divided into corresponuding compartments, each upper compartment and its corresponding lower compartment being connected with a set of the tubes, connections between the compartments whereby [fol. 1082] the oil in circulation may pass from one compartment to another, and supply and residue discharge lines connected with different compartments.

11. A continuous tubular oil still comprising a nest of tubes, upper and lower drums connected with the tubes and divided by diaphragms into compartments, the diaphragms in the upper drum having open communication from compartment to compartment in the upper portion of the drum, a vapor line connected with said upper portion, oil condensing means connected with said line, and supply and residue discharge lines connected with different compartments.

12. A continuous tubular oil still comprising a nest of heating tubes, a drum connected therewith, partitions dividing said drum into comaprtments with openings through the diaphragms toward the bottom of the drum, and supply and residue discharge lines, substantially as described.

13. A continuous tubular oil still comprising a nest of heating tubes, a drum above and connected in circuit with said tubes, and diaphragms in the drum dividing the same into compartments, said diaphragms having open communication between the compartments in the upper part of the drum above the liquid level and having in addition openings below the liquid level.

14. A continuous tubular oil still comprising a nest of heating tubes, an upper drum connected with opposite ends of said tubes, a lower drum connected with the tubes at one end only, diaphragms dividing said drums into compartments, and an oil supply line and a residue discharge line connected with different parts of the still so as to cause

the oil in circulation to progress from compartment to compartment.

15. A continuous tubular oil still comprising a nest of heating tubes, an upper drum connected with opposite ends of said tubes, a lower drum connected with the tubes at one end only, diaphragms dividing said drums into compartments, and connections between adjoining compartments, in combination with an oil supply line, a residue discharge line connected with a remote portion of the still from the supply line, a vapor line leading from the upper drum, and oil condensing means connected with said vapor line.

16. A continuous tubular oil still comprising a nest of heating tubes, and a transverse drum thereabove, said drum being divided transversely into compartments, said compartments communicating with each other, and each compartment connected with opposite ends of a set of the tubes, in combination with supply and residue discharge lines connected so as to cause the oil in circulation to progress from one compartment to another.

17. A continuous tubular oil still comprising a fire-box, a setting, a nest of tubes therein in the path of the products of combustion, a plurality of upper drum compartments connected with opposite ends of said tubes, a plurality of lower drum compartments connected with the tubes at one end thereof, an oil supply line connected with one of the lower compartments, and a residue discharge line connected with a remote upper compartment.

18. A continuous tubular oil still comprising a nest of tubes, upper and lower drums connected therewith, diaphragms dividing the drums into compartments, an oil supply line connected with the first of the lower compartments, an overflow line connected with the last of the upper compartments, and a vapor line connected with the upper drum and leading to an oil condenser.

19. A continuous tubular oil still comprising a nest of tubes, upper and lower drums connected therewith, diaphragms dividing the drums into compartments, an oil supply line connected with the first of the lower compartments, an overflow line connected with the last of the upper com-

partments, a vapor line connected with the upper drum and leading to an oil condenser, and a return line for conducting condensate back to the lower drum.

20. A continuous tubular oil still comprising a nest of tubes, a plurality of upper drum compartments connected in circuit with groups of said tubes in such manner that the oil in circuit may progress from one compartment to another, oil supply and residue discharge lines so connected as to cause such progression, a vapor line, fractional condensing means connected therewith, and a return line for conducting condensate from said condensing means back to the lower portion of the still.

21. A continuous tubular oil still comprising a plurality of communicating sections, each comprising a portion of a nest of tubes and an upper drum compartment connected therewith, and oil supply and residue discharge lines connected with a different sections in combination with a vapor line, fractional condensing means connected with said vapor line, and means whereby condensate may be returned to one or other of said sections as desired.

22. A continuous tubular oil still comprising a plurality of communicating sections, each comprising a portion of a nest of tubes and an upper drum compartment connected therewith, and oil supply and residue discharge lines connected with different sections, in combination with a vapor line, fractional condensing means connected with said vapor [fol. 1083] line, condensate outlets from different portions of said condensing means, and means for returning the condensates to a section or sections of the still or making other disposition thereof as desired.

23. A continuous tubular oil still comprising a nest of tubes, a drum above the tubes divided into compartments connected in circuit with the tubes in such manner that the oil in circulation may progress from one compartment to another, means for supplying the oil to be distilled to one portion of the compound circulatory system constituted by the tubes and compartments, a residue discharge line leading from a drum compartment remote from the supply inlet, oil condensing means connected with the vapor line and a return line from said condensing means to a lower portion of the still.

24. A continuous tubular oil still comprising an inclined nest of tubes connected in tiers between sectional headers, a fire-box below the upper portion of the nest, an upper drum divided into compartments connected with the upper ends of both the front and back headers, a lower drum connected with the lower ends of the back headers, additional circulators extending downward from the upper drum compartments and opening into the lower drum compartments, and means including oil supply and residue discharge lines whereby the oil in circulation is caused to progress from section to section of the still.

25. A continuous tubular oil still comprising a nest of tubes connected in tiers to sectional headers at their ends, a plurality of drum compartments above the tubes, connections between said drum compartments and the upper ends of said sectional headers, additional circulators extending downward from the drum compartments and connecting with the lower portion of the nest of tubes at one end, and means including oil supply and residue discharge lines whereby the oil in circulation is caused to progress from section to section of the still.

26. A continuous tubular oil still comprising a nest of tubes, upper and lower drums divided into compartments connected with the tubes, means including oil supply and residue discharge lines whereby the oil in circulation is caused to progress from section to section of the still, a vapor line leading from the upper drum, an oil condensing means connected with the vapor line, a condensate return line for condensate leading from said condensing means and opening into the bottom of the lower drum, and pumping out means connected with said return line.

27. A continuous tubular oil still comprising a nest of tubes, a drum connected therewith, collapsible diaphragms dividing said drum into compartments, and means including oil supply and residue discharge lines whereby the oil in circulation is caused to progress from one section of the still to another.

In testimony whereof I have signed my name hereto.

Samuel H. Edwards.

Witnesses: Claude K. Edwards, James J. McGrath.

4360

[fol. 1084]

PETITIONER'S EXHIBIT 143

No. 619,593. Patented Feb. 14, 1899.

F. W. MANN.

APPARATUS FOR DISTILLING PETROLEUM.

(Application filed Mar. 20, 1896.)

(No Model.)

Fig. 2.

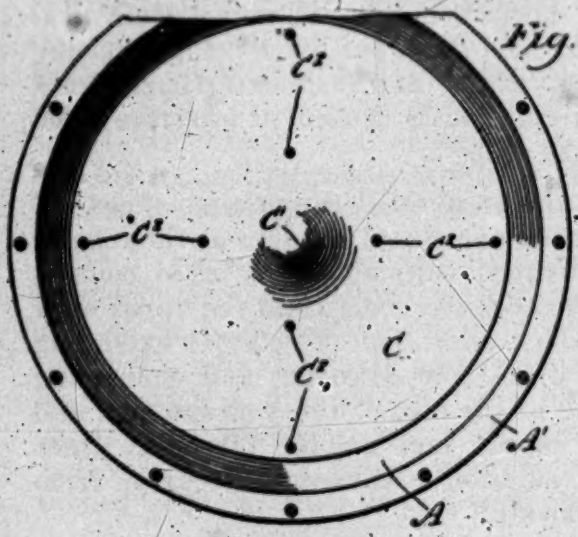
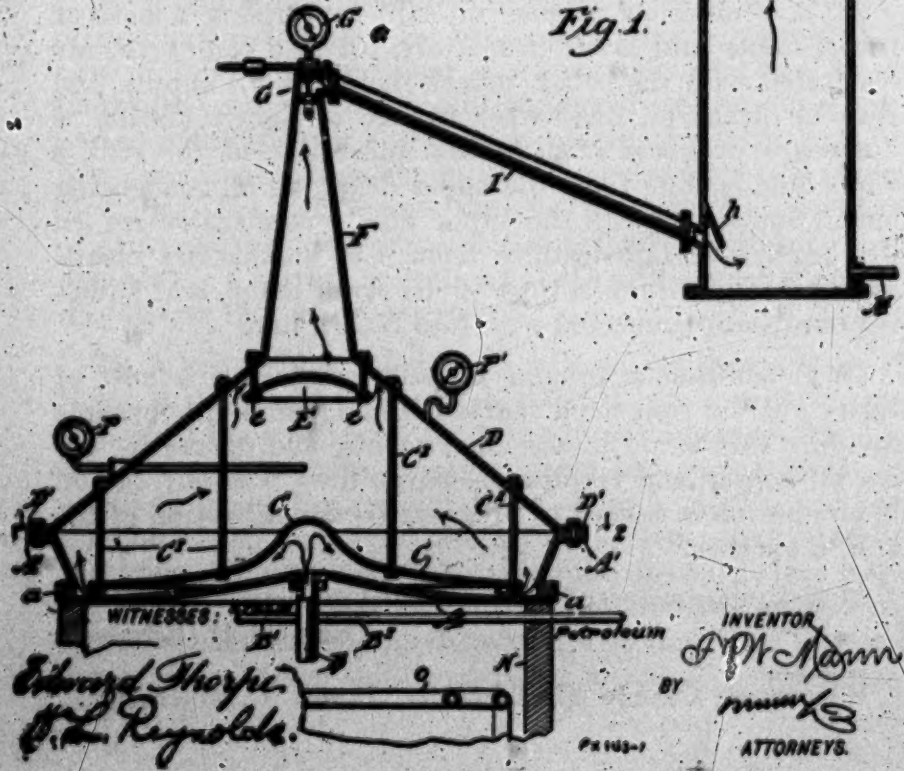


Fig. 1.



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F. W. Mann

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ATTORNEYS.

Px 103-1

[fol. 1085] United States Patent Office

Frederick William Mann, of Franklin, Pennsylvania

Apparatus for Distilling Petroleum

Specification Forming Part of Letters Patent No. 619,593, Dated February 14, 1899

Application filed March 30, 1898. Serial No. 675,699. (No model)

To all whom it may concern:

Be it known that I, Frederick William Mann, of Franklin, in the county of Venango and State of Pennsylvania, have invented a new and Improved Apparatus for Distilling Petroleum, of which the following is a full, clear, and exact description.

My invention relates to certain improvements connected with the distillation of petroleum, and has for its object the production of a larger percentage than hitherto obtained of the lighter hydrocarbon compounds having a greater value than the heavy residue; and it consists of the novel mechanism which will be hereinafter described and claimed.

Reference is to be had to the accompanying drawings, forming a part of this specification, in which similar characters of reference indicate corresponding parts in both the figures.

Figure 1 is a cross-sectional elevation of an apparatus adapted to carry out the process; and Fig. 2 is a cross-sectional view, taken through the distilling-chamber, on the line 2 2 of Fig. 1.

In ordinary process of distilling petroleum there is a considerable residue of the heavy hydrocarbons, which have a relatively small market value. Various processes have been designed for decreasing the proportion of these heavy hydrocarbon compounds. The object of the apparatus herein shown and the process described is to reduce the proportion of these heavy hydrocarbons to a relatively smaller amount than is secured by any of the present processes. One process now in use and known as the "cracking" process submits the hydrocarbon vapors to the action of heat, which breaks up the molecules of the hydrocarbons into other ar-

rangements, resulting in producing a larger proportion of the valuable compounds than by processes preceding it. My process is one which resembles the cracking process; but I have discovered that the results produced by the cracking process may be improved upon by subjecting the hydrocarbon vapors simultaneously to the action of pressure and heat.

I will first describe the apparatus herein illustrated by which my process may be carried out. It is of course understood that other apparatus might be employed for carrying out my process and that the apparatus herein shown is given simply as an illustration of how the process may be carried out.

The distilling-chamber is formed of a shallow cup A, preferably made of cast-iron and with its bottom sloping upward toward the center, so as to produce a flow toward the edge thereof of any liquids which it may contain. This cup is provided with a flange A′, extending about its edge, and also with openings closed by suitable plugs *a* at the lowest point of the cup and acting as drains for discharging the contents of the cup when the cup is to be cleaned. It will not be necessary to provide for drawing off oil from the still while in use, as all the oil will be vaporized and passed over to the condenser. A cone D of relatively small height is provided with a flange D′, adapted to be secured to the flange A′ and thus to form an inclosed chamber. Within this distilling-chamber is a partition-plate C, which is suspended by stay-bolts C^2 from the cone D and is thereby held at a short distance above the bottom of the cup A. In the center of this plate C is formed a pocket C′, which rises above the bottom of the cup A and above the plane of junction of the flanges A′ and D′, thus forming a space of greater width than ordinarily between the partition C and the bottom of the cup A. The distilling-chamber thus formed is heated either by using a sufficient volume of superheated steam introduced into the chamber or by constructing a furnace beneath the chamber. The walls of such a furnace are shown at N. As shown in the drawings, the heat is obtained from gas-pipes O, having perforations therein for the discharge of gas. In lieu thereof it is obvious that ordinary grates or solid fuel may be used.

At the center of the cup A is introduced a short pipe B, through which the hydrocarbons are injected into the distilling-chamber. The pipe B is connected to two pipes B′

and B², one of which is connected with a source of steam-supply and the other with the petroleum-supply. The pipe B serves as a mixing-chamber for the steam and oil. The petroleum is injected into the distilling-chamber as a spray and either with or without the addition of steam. If steam is used, it is preferably superheated steam.

The distilling-chamber is provided with a pyrometer P [fol. 1086] and a pressure-gage P′. To the apex of the cone D is attached a gooseneck F, which is constructed in the form of a conical cylinder. Beneath the opening connecting the gooseneck with the cone D is suspended a plate E by means of bolts *e*, passing through the same and the top of the cone D.

To the upper end of the gooseneck F is attached a pressure-retaining valve G and a pressure-gage G. The pressure-retaining valve may be of any ordinary or preferred construction and is capable of being set so as to maintain the pressure in the distilling-chamber at any point desired and to discharge the contents of said distilling-chamber whenever the pressure exceeds such point. The discharge from the pressure-valve is through a pipe I, which is inclined downward as it extends away from the pressure-valve. This pipe discharges into the lower end of a condenser H. The gases pass upward through the condenser and through a spray of water introduced through the rose or spraying-head K at the top of the condenser. This spraying-head is connected to a pipe extending without the condenser. The gases which have not been condensed by their upward passage through the condenser are discharged through a pipe L into other condensers and are ultimately condensed into oil. The openings of both the pipes I and L are protected by an inclined plate *h* of sheet metal against the water of the spray. The water used for condensing the vapors and the condensed oil is discharged through a pipe M, connected with the lower end of the condenser. The condenser H is provided with suitable gages J and J′.

The operation is as follows: The cast-iron dish or cup of the distilling apparatus is first heated either by gas-jets or by a furnace beneath the same. Through the pipe B a little dry steam is admitted, and the temperature is raised to about 800° Fahrenheit. The pressure-valve G is set so as to retain a pressure of about fifty pounds. The spray of cold water is then started in the condenser. When the apparatus has thus been placed in condition for operation, the

petroleum is injected through the pipe B in the form of a spray, either with or without superheated steam. The vapors of the petroleum coming in contact with the heated dish or cups are thoroughly cracked—that is, the molecules are broken up and reassembled in such form as to produce a larger proportion of the valuable hydrocarbons. These are discharged through the pressure-valve into the condenser. The condensing of the vapors is carried on by any ordinary process. I have herein given the pressure as fifty pounds and the temperature as 800° Fahrenheit, as this pressure and temperature have been found to give good results. I do not, however, wish to be limited to this exact pressure and temperature, as the process may be carried on successfully by varying either pressure or temperature.

By this process an increased production of the lighter and more valuable hydrocarbons may be obtained than by the usual processes of distillation. By this process a larger part of the heavy hydrocarbons may be converted into the lighter hydrocarbons.

Having thus described my invention, I claim as new and desire to secure by Letters Patent—

1. A petroleum-distilling apparatus, comprising a closed vessel having a portion thereof adapted to be heated, a partition within the vessel lying close to such heated surface, means for introducing a petroleum-spray into the space between said partition and the heated surface of the vessel, and means for maintaining a uniform pressure in said vessel, substantially as described.

2. A petroleum-distilling apparatus, comprising a closed vessel having a portion thereof adapted to be heated, a partition within the vessel lying close to said heated surface, means for introducing a petroleum-spray into the space between the said partition and the heated surface of the vessel, and a pressure-valve controlling the discharge from said vessel, substantially as described.

3. A petroleum-distilling apparatus, comprising a closed vessel having a portion thereof adapted to be heated, a partition within the vessel lying close to said heated surface, means for introducing a petroleum-spray into the space between the said partition and the heated surface of the vessel, a pressure-valve controlling the discharge from said

vessel, and a condenser connected to said discharge, substantially as described.

4. A petroleum-distilling apparatus, comprising a closed vessel having a portion thereof adapted to be heated, a partition within the vessel lying close to said heated surface and at its center having a pocket which increases the distance between the partition and the vessel-wall, a petroleum-spray discharging into said pocket, and a pressure-valve controlling the discharge from said vessel, substantially as described.

5. A petroleum-distilling apparatus, comprising a closed vessel having a portion thereof adapted to be heated, a partition within the vessel lying close to said heated surface means for introducing a petroleum-spray into the space between the said partitions and the heated surface of the vessel, a pressure-valve controlling the discharge from said vessel, and a condenser connected to said discharge, and having a water-spray discharging into its upper end, substantially as described.

Frederick William Mann.

Witnesses: Hiram Brown, Samuel Cooper.

[fol. 1087] PETITIONER'S EXHIBIT 144

No. 25,510. (Coat of Arms.) A. D. 1913

Date of Application: 7th Nov., 1913. Accepted: 1st July, 1915

Complete Specification

Process for Obtaining Light Hydrocarbons from Heavy Hydrocarbons

We, Dr. Edmund Graffe, of Bayreuther-strasse 16, Dresden A., Saxony, and Professor Dr. Reinhold Freiherr von Walther, of Munchner-strasse 15, Dresden A., Saxony, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:

The problem of transforming heavy hydrocarbons into light ones is of the greatest technical and economical importance. On the one hand constantly increasing quantities of low-boiling hydrocarbons are needed, in consequence of the ever-growing demand for these products, above all of gasolene for driving automobiles and of solvents; whereas on the other hand, notwithstanding the greatly increased production of crude petroleum, the production of oils which contain a great number of such light hydrocarbons is constantly decreasing because a great amount of the crude oils obtained to-day are of a heavy asphaltic nature. The price of gasolene is still on the increase, while on the other hand the heavy asphaltic oil residues are to be had to a low price. Even before the problem of obtaining light hydrocarbons was so pressing many attempts were made to transform the heavy petroleum distillates or residues into lighter ones. At first the intention was to obtain illuminating oil, which at that time was the most valuable and desired product. As early as the year 1865 Young proposed to distil heavy oils under pressure (British Patent 3345 of 1865). The same object is aimed at in British Patent 1697 of 1866. The pressures used were comparatively low, and only amounted to about 1 to 2 atm. Krey (German Patent 37,728 of 1886) had the same goal in view when he distilled paraffin oils and petroleum residues under pressure of about 2 to 6 atm. He obtained by this means on the one hand an increased yield of illuminating oil and on the other hand residues of a lubricant character [fol. 1088] or asphalt. Similar pressures were used by Benton (U. S. Patents 342,564 and 342,565 and British Patent 1922 of 1887) who distilled at a pressure of about 285 lbs. per square inch. Benton himself did not heat the oil vapours under pressure but only the oil in a heated coil; then allowing it to evaporate in a chamber under atmospheric pressure (see English Patent No. 1922 of 1887). Dewar and Redwood (German Patent 53,552, British Patent 10,277 of 1889) similarly distilled under pressure, at the same time however conducting air or other inert gas under pressure into the distilling apparatus during the distillation. Similar to the process of Dewar and Redwood, who work with the aid of inert gases are the processes of Halcour

and Pilgram (German Patent Application Class 23 B L 32,413) and Leffer (Belgian Patent 242,628 and British Patent 2328 of 1912), who also introduce inert gases during the distillation for purposes of pressure, such gases serving for keeping the pressure, viz., about 10 to 12 atm. steady and constant. The oils to be distilled may at the same time be stirred or otherwise agitated and the temperature may not exceed 410° C.

Testelin and Renard also work with pressure, using however steam for this purpose (German Patent Application T. 13,287 Class 23b and British Patent 16,881 of 1908), and conducting the steam mixture over a layer of red hot alumina or other similar substance.

A further patent of Auguste Testelin and Georges Renard of Brussels (German Patent No. 226,958 Class 23b, and corresponding British Patent 3413 of 1913) also has the object of producing low boiling hydrocarbons by heating under pressure and with correspondingly high temperature. With this process, however, the material under treatment is not under its own vapour pressure, but under an artificial pressure, exceeding the vapour tension of the oil.

It has also been proposed (British Specification No. 29,862 of 1912 Wade) to obtain light hydrocarbons of the character of petrol by distilling heavy oils under the comparatively low pressure of 4 to 5 atmospheres. The second part of the process described in the said specification represents a distillation of the residues of the pressure-distillation under atmospheric pressure, with the aid of steam:

[fol. 1089] It will be seen from the above, that:

(1) Oils have on the one hand already been distilled under their own, but low vapour pressure.

(2) Heavy hydrocarbons have also been distilled under higher pressure, which in this case however was brought about by inert gases; and

(3) Hydrocarbons have been heated under high pressure without any simultaneous distillation.

The present process differs from those described above under (1) by maintaining a very much higher steam pres-

sure than used with the known processes during distillation; from those under (2) inasmuch as the pressure is not obtained artificially by inert gases, but by the tension of the vapour or gas itself, corresponding to the temperature used; and from those under (3) inasmuch as under the said high pressure a transformation into vapour, i. e., a distillation, takes place.

It has been found that by the new process a greatly increased yield of gasolene is obtained, which, considering the present state of the market is far more important than the yield of illuminating oil.

This increased yield of gasolene was not at first sight to be expected; indeed there was rather reason to fear, as seemed to be the case of the higher limits of temperature in some of the above-mentioned patents, that by increasing the temperature a different decomposition would take place, by which, instead of aliphatic hydrocarbons, aromatic or terpene-hydrocarbons would be obtained.

As ray material for the production of light hydrocarbons by the present process, heavy hydrocarbons are taken.

More particularly this process for obtaining light hydrocarbons consists in bringing the oils by means of high temperatures up to a high vapour pressure of their own, viz., about 20 to 50 atm., and maintaining this high vapour pressure while distilling the same.

The temperatures used with these high pressures of 20 to 50 atm. depend on the oils used. The higher the pressure and temperature employed, the greater will be the yield of light hydrocarbons.

A further modification of the process consists in submitting the gases and vapours produced to high pressure in a large heated gas or vapour chamber, only letting them off and condensing them after a time sufficiently long for their decomposition has elapsed. These large gas or vapour chambers may be situated within the distilling apparatus itself.

[fol. 1090] By means of using these large gas and vapour chambers the gases and vapours produced will remain for a long period in intimate contract with each other under high pressure. This is for the purpose of ensuring that the hydrogen partly generated during the decomposition

will as much as possible combine with the unsaturated hydrocarbons which are the result of the decomposition: for it is known that gas reactions which take place under decrease of volume which is the case when hydrogen is absorbed, are favourably influenced and accelerated by increased pressure. When hydrogen is absorbed the amount of unsaturated hydrocarbons is decreased, whereby the quality of the products is raised. The presence of inert gases, for the purpose of furthering the gas reactions, should if possible be avoided, as they only effect a dilution. For this reason it is even preferable to exhaust the distilling apparatus before commencing the distillation. The oils are then heated until the desired pressure of about 20 to 50 atm. is reached, whereupon the resulting decomposed products are let off and conducted to the condenser, the distillation taking place while the high pressure is maintained as constant as possible. Naturally it will be desirable to supply new raw material continuously to the distilling apparatus, and to conduct the distillation only so far as allows of a liquid residue remaining, and to continuously draw the latter off.

Furthermore, the principles of fractionated distillation may be applied to the present process of distillation under pressure, in such a manner that a number of decomposing distilling apparatus be arranged in series and the contents of each of the same be made to flow to the next one, whereby steady pressures and temperatures, otherwise only difficulty obtainable, are procured.

The temperatures used with this present process are not at all limited in regard to their height, but depend solely on the pressure desired. However, a super-heating of the gas and vapour chambers should be avoided, so that as few aromatic hydrocarbons as possible may be produced. The gas as it leaves the condenser is compressed by degrees. The condensates separating out during the first degree of compression are obtained as petrol-ether; those produced under higher compression as liquid illuminating gas, such as the so-called "blaugas." The remainder not capable of further condensation is used as heating, illuminating, or motor gas.

The best raw material is the residue of the crude oil dis- [fol. 1091] tillation having the highest possible boiling point and being quite free from gasolene and illuminating oil. The process is particularly applicable in connection with oil residues having a long open chain, such as residues of German, Californian, Mexican, or Galician oil.

The accompanying drawings illustrate by way of example a form of decomposing distilling apparatus suitable for the purpose of the invention, Fig. 1 being a longitudinal section and Fig. 2 a cross section thereof.

a represents a boiler-like autoclave connected to a pressure pump by the pipe *b* fitted with a valve b^1. *c* is a thermometer, *d* a manometer, and *e* a pipe fitted with a valve e^1, for removing the residue formed. *f* is a lead bath for obtaining uniform heating. *g* is a discharge pipe fitted with a valve g^1, for the vapours and *h* is a safety valve.

In operation with this apparatus, the pressure is obtained simply by leaving the valve in the vapour discharge pipe screwed up until the pressure has risen to the desired amount of between 25 and 50 atmospheres, and then under continued heating of the autoclave the position of the valve is adjusted so that only such a quantity of vapours and gases pass off from the autoclave that the pressure remains at the desired value. In apparatus with a separate vapour space or chamber the pressure is kept uniform or regulated by only regulating the valve leading from the vapour space to the condenser and leaving the other one, that between the autoclave and the vapour space, open.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:

1. Process for obtaining light hydrocarbons, consisting in bringing the oils or petroleum by means of high temperatures to a high vapour pressure of their own of about 20 to 50 atm. and distilling the same under maintenance of the high vapour pressure thus obtained.

2. Process for obtaining light hydrocarbons according to Claim 1, consisting in maintaining the gases and vapours produced at a high pressure in large heated gas or vapour chambers, and only letting them off and condensing them

after a time sufficiently long for their decomposition has elapsed.

3. Process for obtaining light hydrocarbons according to Claims 1 and 2, consisting in arranging the large gas or vapour chambers within the distilling apparatus itself.

[fol. 1092] 4. Process for obtaining light hydrocarbons, according to Claims 1, 2 and 3, consisting in applying the principles of fractionated distillation to the present process of distillation under pressure herein claimed, in such a manner that a number of decomposing distilling apparatus are arranged in series and the contents of each one of the same made to flow to the subsequent one, whereby steady pressures and temperatures, otherwise only difficulty obtainable are maintained.

Dated this 7th day of November, 1913.

Newburn, Ellis & Pryor, 70 & 72, Chancery Lane, London, W. C., Chartered Patent Agents.

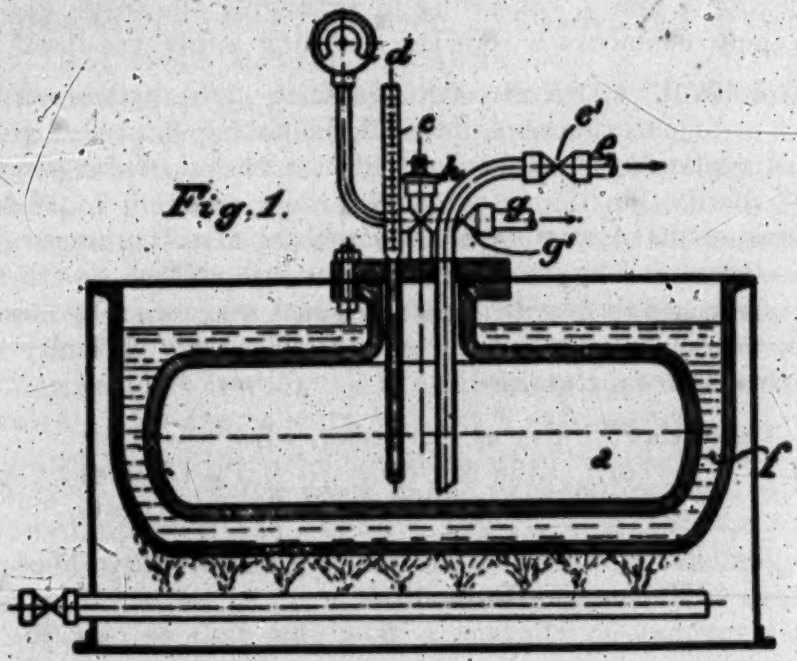
Redhill: Printed for His Majesty's stationery Office, by Love & Malcomson, Ltd.—1915.

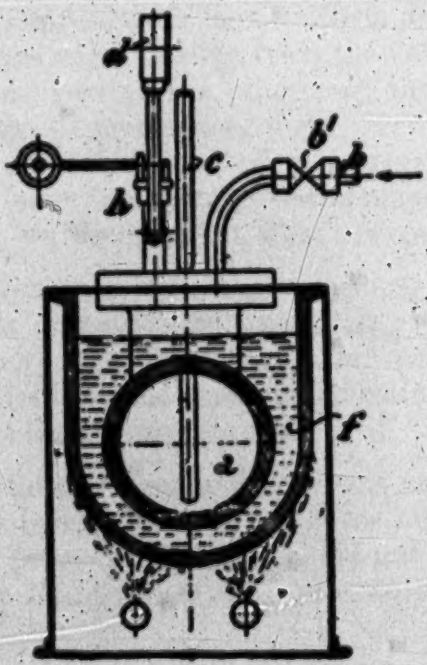
[fol. 1093]

A.D. 1913. Nov. 7 N° 25,510.

J. AEPE & another's COMPLETE SPECIFICATION. (1 SHEET)

Fig. 1.





[fol. 1094]

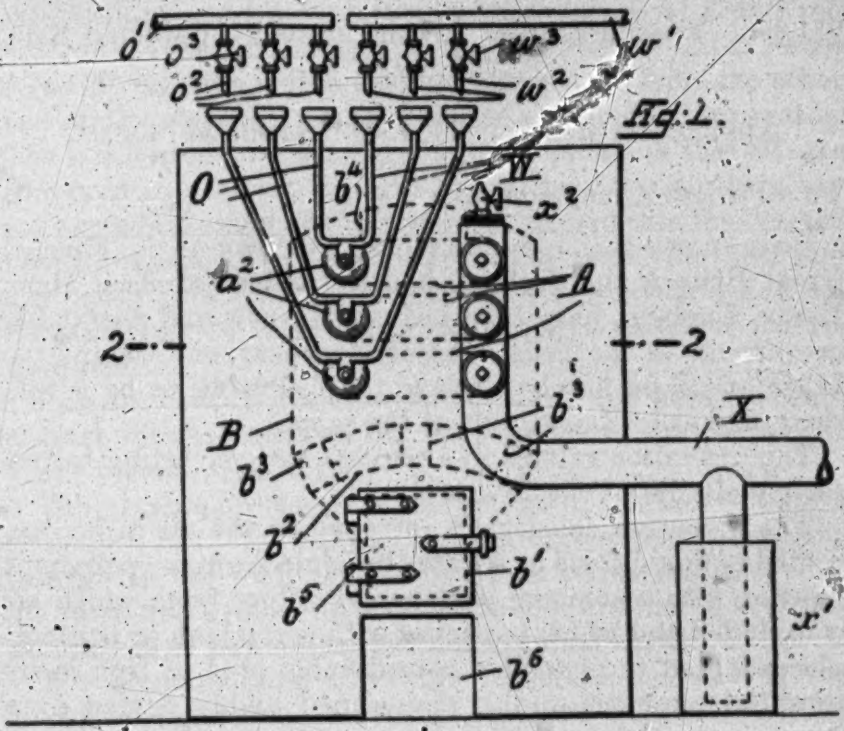
PETITIONER'S EXHIBIT 145

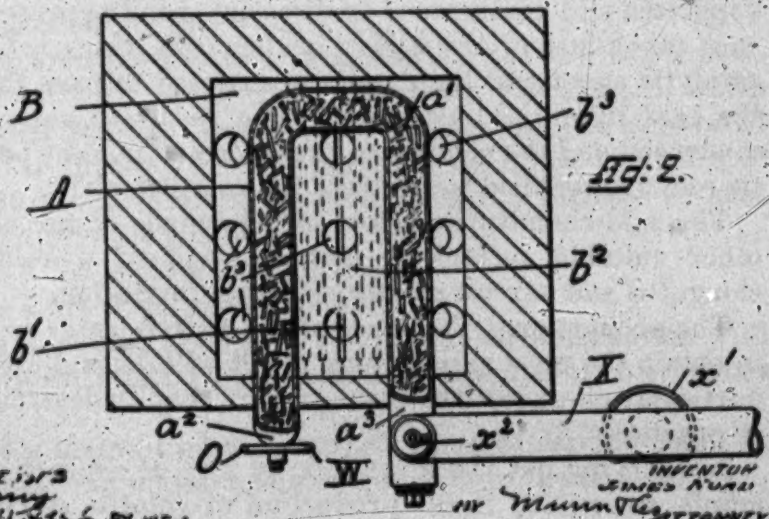
J. NOAD.

TREATMENT OF HYDROCARBON OILS AND THE LIKE.

APPLICATION FILED JULY 11, 1908.

971,468. Patented Sept. 27, 1910.





WITNESSES
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INVENTOR
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ATTORNEYS

PX 145-1

[fol. 1095] United States Patent Office

James Noad, of East Ham, England, Assignor of One-Half to Edward Joseph Townsend, of London, England

Treatment of Hydrocarbon Oils and the Like

971,468. Specification of Letters Patent. Patented Sept. 27, 1910

Application filed July 11, 1908. Serial No. 443,092

To all whom it may concern:

Be it known that I, James Noad, a subject of the King of Great Britain and Ireland, and a resident of East Ham, Essex, England, have invented certain new and useful Improvements in the Treatment of Hydrocarbon Oils and the Like; and I do hereby declare the following to be a full, clear, and exact description of the same.

This invention relates to a process for converting hydrocarbon oils into volatile spirit.

The invention consists in introducing the oil to be converted in liquid form and water in liquid form in contiguous relation into a common chamber or retort from which air is excluded and which is packed with scrap iron or is otherwise adapted to present a considerable area of iron in interstitial passages and is maintained highly heated by a furnace or other suitable means, so that such liquids are vaporized and decomposed or dissociated in the presence of each other and of the highly heated iron which acts as a catalytic agent and the vapors are caused to pass through the said interstitial passages. The resultant vapors are condensed and the condensed products or the light portions thereof are rectified to separate the volatile spirit.

The said chamber or retort may be made of fire clay or other suitable refractory material and of a relatively elongated and narrow or other suitable formation.

The proportional quantities of the oil and water required to obtain the most satisfactory result will depend upon the particular oil under treatment and are readily determinable in practice.

In carrying out the invention, by way of a practical example, as applied to the production of volatile spirit suit-

able for use in internal combustion engines, from North American solar oil of about .863 s. g. The oil to be converted and water are fed from separate reservoirs and are contiguously dropped or passed in fine streams, in approximately the proportions of 2 parts of oil to 1 part of water, into one end of a closed chamber or retort packed as aforesaid with loose or scrap iron and maintained at a dull red heat, say, about 900° Fahrenheit. The vapors which result from the reaction within the chamber are led from the other end of the chamber to any suitable condensing apparatus. The condensed products or the light portions thereof are conveyed to a rectifying still heated to a temperature say not exceeding about 300° Fahrenheit to separate the desired volatile spirit. The residue from the rectifying still and any heavy products that may have been condensed and not rectified may be returned to the reaction chamber for retreatment.

I do not broadly claim bringing steam and heavy oil into contact with heated iron for the purpose of converting the heavy oil into light oil.

The present process is of advantage in relation to known processes, in that it enables a much higher percentage and practically the whole of the oil to be converted into volatile spirit and avoids the production of more than a very low percentage of permanent gas and residual carbon.

The accompanying drawings illustrate, by way of example, an apparatus suitable for carrying out the invention.

Figure 1 is a front elevation; and Fig. 2 is a plan, partly in section on the line 2—2, Fig. 1.

A, A, are closed retorts packed with loose or scrap iron a^1. The retorts are mounted in a fireproof chamber, B, which is heated by a furnace, b^1. The chamber B is separated from the furnace, b^1 by a partition b^2, which has holes b^3 for the products of combustion from the furnace to pass through into the chamber.

b^4 is a flue leading to the chimney.

b^5 is a fire door, and b^6 an ash pit.

The inlet end, a^2 of each retort is in communication with two branch pipes, O, W, made funnel-shape at their upper ends.

o^1 is a main fitted with branch pipes, o^2, having cocks o^3, for supplying oil in regulable quantity to the pipes O.

w^1 is a main fitted with branch pipes, w^2 having cocks w^3, for supplying water in regulable quantity to the pipes W.

The outlet ends, a^2 of the retorts are in communication with a main X, for leading the vapors to suitable condensing apparatus.

x^1 is a water seal, and x^2 is a test cock.

What I claim is:

[fol. 1096] The process of converting mineral oil into petroleum spirit, consisting in introducing the oil in liquid form and water in liquid form in contiguous relation into a retort, decomposing or dissociating the oil and water by allowing them in contiguous relation to come into intimate contact within said retort with iron heated to a temperature of about 900 degrees Fahrenheit, and leading off the resultant vapor products to a condenser, substantially as described.

In testimony whereof I affix my signature, in presence of two subscribing witnesses.

James Noad.

Witnesses: Charles Aubrey Day, William Arthur McMullen.

[fol. 1097] PETITIONER'S EXHIBIT 146

No. 13675. (Coat of Arms) A. D. 1908

Date of Application: 27th June, 1908. Accepted: 7th Jan., 1909

Complete Specification

Improvements in the Treatment of Hydrocarbon Oils or the Like for the Production of Volatile Spirit

We, James Noad, of 4 Grove Villas, High Street, East Ham, Essex, Engineer, and Edward Joseph Townsend, of 52 Queen Victoria Street, E. C., Accountant, do hereby declare the nature of this invention and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement.

This invention relates to a process for converting hydrocarbon oils, or the like, hereinafter referred to as oil, into volatile spirit.

The invention is characterized by introducing the oil to be converted in liquid form and water in liquid form in contiguous relation into a common chamber or retort from which air is excluded and which is packed with scrap iron or is otherwise adapted to present a considerable area of iron in interstitial passages and is maintained highly heated by a furnace or other suitable means, so that such liquids are vaporized and decomposed or dissociated in the presence of each other and of the highly heated iron which acts as a catalytic agent and the vapours are caused to pass through the said interstitial passage. The resultant vapors are condensed and the condensed products or the light portions thereof are rectified to separate the volatile spirit.

The said chamber or retort may be made of fire clay or other suitable refractory material and of a relatively elongated and narrow or other suitable formation.

The proportional quantities of the oil and water required to obtain the most satisfactory result will depend upon the particular oil under treatment and are readily determinable in practice.

In carrying out the invention, by way of a practical example, as applied to the production of volatile spirit suitable for use in internal combustion engines, from North [fol. 1098] American solar oil of about .863 s. g.—The oil to be converted and water are fed from separate reservoirs and are contiguously dropped or passed in fine streams, in approximately the proportions of 2 parts oil to 1 part of water, into one end of a closed chamber or retort packed as aforesaid with loose or scrap iron and maintained at a dull red heat, say, about 900° Fahrenheit. The vapours which result from the reaction within the chamber are led from the other end of the chamber to any suitable condensing apparatus. The condensed products or the light portions thereof are conveyed to a rectifying still heated to a temperature say not exceeding about 300° Fahrenheit to separate the desired volatile spirit. The residue from the rectifying still and any heavy products that may have been condensed and not rectified may be returned to the reaction chamber for retreatment.

The process is of advantage in relation to known processes, in that it enables a much higher percentage and practically the whole of the oil to be converted into volatile spirit and avoids the production of more than a very low percentage of permanent gas and residual carbon.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, we declare that we do not broadly claim bringing steam and heavy oil into contact with heated iron for the purpose of converting the heavy oil into light oil, but that what we claim is:

1. In the conversion of oil into volatile spirit, the treatment characterized by the fact that the oil to be converted in liquid form and water in liquid form are vaporized and decomposed or dissociated in the presence of each other and of highly heated iron in form adapted to present a considerable area of iron in interstitial passages, all with the exclusion of air, substantially as described.

2. The process for converting oil into volatile spirit, consisting in introducing the oil in liquid form and water in liquid form in contiguous relation into a common chamber or retort from which air is excluded and which is adapted to present a considerable area of iron in interstitial passages and is maintained highly heated by a furnace or other suitable means so that such liquids are vaporized and decomposed or dissociated in the presence of each other and of the highly heated iron and the vapours are caused to pass [fol. 1099] through the said interstitial passages, condensing the resultant vapours, and rectifying the condensed products or the light portions thereof to separate the volatile spirit, substantially as described.

Dated this 24th day of June, 1908.

Day, Davies & Hunt, Chartered Patent Agents, 321, High Holborn, London, W. C., Agents for the Applicant.

Redhill: Printed for His Majesty's Stationery Office, by Love & Malcomson, Ltd.,—1909.

PETITIONER'S EXHIBIT 147

No. 16,881. (Coat of Arms.) A. D. 1908

Date of Application: 11th Aug., 1908. Accepted: 3rd June, 1909

Complete Specification

Improved Apparatus for the Industrial Manufacture of a New Spirit by the Treatment of Petroleum

We, Auguste Testelin, of No. 304 Rue des Palais, and Georges Renard, of No. 125, rue du Trone, both of Brussels, Belgium, Engineers, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:

This invention relates to the manufacture of spirit by the treatment of petroleum, and has for its object to obtain a new spirit of an ethereal, penetrating and characteristic odour, quite distinct from the odour of petroleum of which no trace remains, the new spirit being also highly refractive, very mobile, volatile and inflammable, and having a particularly wide solvent power.

The apparatus included in this invention is in its main parts similar to apparatus heretofore used, and consisting of a force pump for the hydrocarbon fluid, a steam generator, a coil to which the hydrocarbon vapour and steam are conducted, a retort leading from the coil, and finally a fractionating condenser.

[fol. 1100] Apparatus of this type has been proposed for the continuous distillation, boiling, saponification, and acidification of fats, oils, glycerine, rosins, and hydrocarbons such as paraffin or ozokerit, whereby the hydrocarbons from a tank were permitted to enter an injector with some pressure, stop cocks being used to regulate the flow of steam and of the fat etc. A metal coil was connected with the injector and entered a horizontal retort divided by partitions, in such a way that steam and vapours introduced at the outlet of the coil were obliged to circulate forward and backwards inside the retort, the inside of the retort being by preference filled with coarse pieces of coke or

brick. The fats etc., being atomized by the steam presented an immensely extended surface; distillation, therefore, taking place with the greatest possible rapidity and at a low temperature; and only small quantities of fat etc., were at any one time under the influence of heat and then only for the very shortest possible time. It has also been proposed with similar apparatus to produce a lighter oil of uniform gravity from hydrocarbon or other oils.

Now the present invention aims, as already stated, at the production of a new spirit, and an important feature of the apparatus hereinafter described is the means for directing and controlling the superheated vapours and steam, the regulation of their pressure and their temperature.

For this purpose, according to the present invention, the furnace is so devised that the retort is constantly maintained at a red heat, while the coil is never allowed appreciably to exceed 400° to 450° Centigrade; the tubes and cocks which control the superheated vapour and steam are so arranged that said vapours and steam can be directed at will either directly to the fractionating and condensing apparatus, or through the retort; said retort is provided for a small distance only with the burnt porous clay; between the retort and coil and the fractionating apparatus, there are arranged an air chamber, an automatic regulator and a pressure gauge for constantly maintaining the predetermined pressure; and finally, the force pump, which is of small capacity, sends the liquid before passing to the coil, into a closed reservoir having a pressure gauge, a gauge glass, inlet cock, regulating outlet cock and non-return valve, through which last is forced air compressed to the predetermined pressure of five atmospheres. Preferably, the plant for the fractionation and condensation [fol. 1101] comprises; a reflux still, a set of analyser columns and a cold coil, together with an escape chimney.

Besides the phenomena of distillation, it is possible to produce, by the aid of this apparatus, isomeric transformations and products of decomposition.

The illuminating petroleum of commerce, suitably treated in this apparatus, undergoes more or less profound modifications according to the pressure and the intensity of the heat applied.

It has been ascertained that the liquid after being subjected to distillation and fractionated, has changed in density. Light hydrocarbons have been formed simultaneously with heavier congeners. By passing the heavy products through the apparatus again, they are finally transformed into light spirit. The relative proportion of these bodies is dependent upon the pressure, the degree of superheating and the duration of the contact of the petroleum in this medium.

By pushing the superheating until there is a slight appearance of gaseous, that is to say, uncondensible hydrocarbons, the greatest quantity of light products, such as the gasoline kind, etc., is obtained.

In all cases, there is no appreciable loss on the total quantity of petroleum started with.

In the drawings annexed to this specification:

Fig. 1 is a diagrammatic view of the whole of the plant.

Fig. 2 is a plan view of the furnace.

Fig. 3 is front view of the furnace, the masonry being supposed to be removed.

The plant for the fractionation and condensation of the new spirit is composed of a reflux still A and a set of analyser columns B B^1 and B^2 terminating in a cold coil C for complete condensation provided with an escape chimney D for carrying off any gaseous emanations which may have formed during any irregularity in the heating.

The apparatus consists of a furnace E in which are arranged straight iron tubes F placed horizontally alongside each other but leaving between them a free space about equal to their diameter, the tubes F being connected at the ends by elbows, thus forming a single pipe. Into this sort of coil is directed a jet of steam under high pressure, which serves to carry along and superheat the liquids operated upon. To this end the entrance of the tubular system is provided with an aspirating injector G through which passes the steam while carrying along the petroleum to be distilled.

[fol. 1102] Suitable cocks and a needle valve in the pipe permit of a perfect regulation of the relative quantities of steam and petroleum.

In the pipe leading from the coil and retort to the fractionating device are arranged an air chamber H, and an

automatic regulator H', which maintains the necessary pressure; a pressure gauge I completes this apparatus.

The tubes F are fitted with screw stoppers at each end for the purpose of enabling them to be cleaned in case of need.

In the same furnace and below the coil is placed horizontally a tube of cast iron J, or larger diameter traversing the furnace from side to side. This tube J performs the office of transformation retort and is connected by one of its ends to the coil; the other end leads to the condensation apparatus.

The tubes J and F are so arranged in the furnace that the tube J may be constantly heated to a red heat, while the system of tubes F above it is never brought to a degree of heat appreciably exceeding 400° to 450° Centigrade. The arrangement of tubes K and cocks allows the superheated vapours to be directed at will, either directly to the fractionating and condensing apparatus, or to be passed through the red hot tube J before they pass to the pipe leading to the condensers.

The tube J is filled for part of its length with small crushed pieces of burnt porous clay, the filling forming a diaphragm permeable by the vapours of the gaseous hydrocarbons.

Finally the supply of the petroleum is carried out continuously by the aid of a small suction and force pump L, which sends the liquid into a closed reservoir M having a pressure gauge N and a gauge glass O, inlet cock P and regulating outlet cock Q, also a non-return valve R through which air is forced compressed to five atmospheres.

A tube S of small diameter provided with a cock conducts the liquid to the injector of the superheating coil.

To work this plant, the furnace of the superheating apparatus is first lighted, then a current of steam from a boiler, at a pressure of five atmospheres, is passed in solely through the superheating coil and thence directly to the condenser.

As soon as the piping and the whole apparatus is sufficiently hot, and the water, condensed in the final cooler, commences to run away, the supply of petroleum is slightly opened, and the feed of steam and petroleum must be so regulated relatively to each other, that the condensation of

[fol. 1103] the volume of water and petroleum which distils is practically equal in quantity.

This gives the distillation pure and simple of the petroleum with the fractionation of the heavy portions and of the lighter spirits, as they formerly existed in the product operated upon.

The passage to the red hot retort or tube J is opened for the vapours of water and petroleum, and then the direct passage of these vapours to the condensing apparatus is shut off immediately afterwards.

In passing through the red hot porous mass of burnt clay in the retort, the petroleum undergoes a very complex modification; incondensible gaseous hydrocarbons are evolved simultaneously with a series of hydrocarbons which are condensible into liquids of divers densities which run from 600° to the density of the liquid itself operated upon.

It is here that the conditions which determine or modify the pyrogen-ous reactions apply, i. e. the influence of pressure, degree of temperature and the duration of this pyrogenitic action.

Under the conditions of installation and working set forth above, the influence of the catalytic bodies exercises a leading effect, (petroleum is a mixture of a number of hydrocarbons which, under these conditions, play the part of catalytic bodies towards one another), which is the more accentuated, since, in the retort, the partition of burnt porous clay brought to a red heat, diffuses and treats the petroleum vapours continually renewed. This rapid circulation carries the modified hydrocarbons beyond the action of the fire and withdraws them from a more complete destruction.

In this operation of simultaneous distillation and transformation of the petroleum, not only are hydrocarbons formed which are lighter than the initial product, but this latter has disappeared; a new spirit has been formed of an ethereal penetrating and characteristic odour, altogether different from the odour of petroleum of which no trace remains.

The new spirit is highly refractive very mobile, very volatile and extremely inflammable; its solvent power is particularly wide.

Commercial practice has demonstrated that the dominant question has always been: a very high degree of heat,

either a dull red heat to obtain heavy liquid products, or a more intense red heat which yields the lightest products up to those which are gaseous and incondensible.

[fol. 1104] The operator should maintain an equal heating, determined once for all.

In like manner, there must be perfect regulation in the circulation of the steam and the injection of the petroleum.

For a given intensity of heating therefore, the supply of steam or petroleum cannot be varied, thus there would be sensible cooling down of the entire superheating system, by augmentation of the supply as also superelevation of the temperature in case of diminution of the supply feeding the apparatus.

In the first case only little or no light spirit would be obtained, and in the second, an abundant evolution of gas would be produced from which there would necessarily be a loss of spirit.

By applying these principles in a manner well understood, the effects will be reversed when necessary by augmenting the feed supplies at the moment of too strong a heating and by diminishing them in the contrary case.

With regard to the pressure to be maintained in the superheating apparatus regulation will likewise be necessary.

The intervention of this pressure accentuates the modificatory action of the heat and serves to obtain the result desired by raising as little as possible the degree of heat while yet effecting a sufficiently profound molecular transformation.

It should be remarked that the pressure in the apparatus is not established in an exact and regular manner. It is rather a mean of variations formed by sudden leaps repeated without cessation, a species of sudden detonations.

The air chamber H placed near the pressure regulator has the effect of deadening these shocks.

The special arrangements of the apparatus allow of easy manipulation of all the parts which regulate and modify at will the conditions of working.

The capacity of the superheating apparatus occupying only a very restricted space, and the petroleum being supplied thereto by a small atomised drop, it is possible at any instant to take away from the condenser test portions which indicate the progress of the work in the retort; at the same

moment it is easy to immediately modify this progress by opening the supply of petroleum or steam more or less, to regulate the pressure, the intensity of the fire etc.

The principal uses of the spirit obtained by this process are:

[fol. 1105] Automobile motors, where its place is quite indicated by the power of the explosion of the mixture of carburetted air.

Varnishes and colours; by its great solvent power.

Extracting agent; in commerce for autoclave apparatus, displacement apparatus etc.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:

Apparatus for the manufacture of a spirit by the treatment of petroleum comprising a retort constantly maintained at a red heat and a coil at a heat not appreciably exceeding 400° to 450° Centigrade, means whereby said vapour and steam can be directed either to the fractionating and condensing apparatus or to the retort, an air chamber, an automatic regulator and a pressure gauge, interposed between the retort and coil and the fractionating apparatus, a closed reservoir having a pressure gauge, a gauge glass, inlet cock, a regulating outlet cock and a non-return valve through which last can be forced air compressed to the predetermined pressure of five atmospheres; substantially as described.

Dated this 11th day of August 1908.

Brewer & Son, 33, Chancery Lane, London, and 7, East Parade, Leeds, Patent Agents for the Applicants.

Redhill: Printed for His Majesty's Stationery Office, by Love & Malcomson, Ltd.—1909.

[fol. 1106] TRANSLATION OF PETITIONER'S EXHIBIT No. 148

(546)

Zeitschrift fur Angewandte Chemi., p. 546

W. N. Oglobin. The Description of Benzol and its Homologies from Russian Naphtha According the Process of A. N. Nikiforoff. (See Dye and Textile Industry 3, 293, for Aug. 15, 1905. Iwanowo-Wosnessensk)

By this process naphtha (best of all raw naphtha, but also residues) is first subjected under ordinary pressure to a temperature of 525-550° and following this, under two Atm. (Atmospheres) pressure to a temperature of about 1200°. Hereby, due to cleavage of H, benzol and its homologies develop from the naphthas. Following the first operation the naphthalenes are to be split into 3 fractions; 1. tar (about 35%, bpt. >220?) 2. hydrocarbons, so-called "useful tar" (about 27-32%, bpt. <200°), 3. gases (13-18%). Fraction 2 (specific weight 0.84-0.88) is subjected to operation 2, whereby again 3 fractions result: 1. the heavy parts, 2. the light parts, 3. the gases. Fractions 2 and 3, so-called "aromatic tar," are re-distilled. Thereby one derives as one part, up to 120°, "gray benzol" (yield about 12%), containing besides benzol (58%) also toluol (28%) and xylole, while the higher parts up to 200°, are again subjected to decomposition under pressure; From the fractions above 200°, naphthalene (2-3% raw naphtha) and anthracene (1%) can be obtained. According to Zielinski, the hydrocarbons derived from Russian naphtha are free from thiophene and its homologies, as well as from hydro derivatives, acids and phenol, hence, needing no chemical purification. According to the author, the good yields, above all of benzol (>6% of raw naphtha), open technical possibilities for the process.

[fol. 1107]

PETITIONER'S EXHIBIT 149

No. 755,309. PATENTED MAR. 22, 1904.

A. NIKIFOROFF.

MANUFACTURE OF THE BENZOLS AND THEIR HOMOLOGUES.

APPLICATION FILED SEPT. 8, 1902

NO MODEL. 3 SHEETS—SHEET 1.

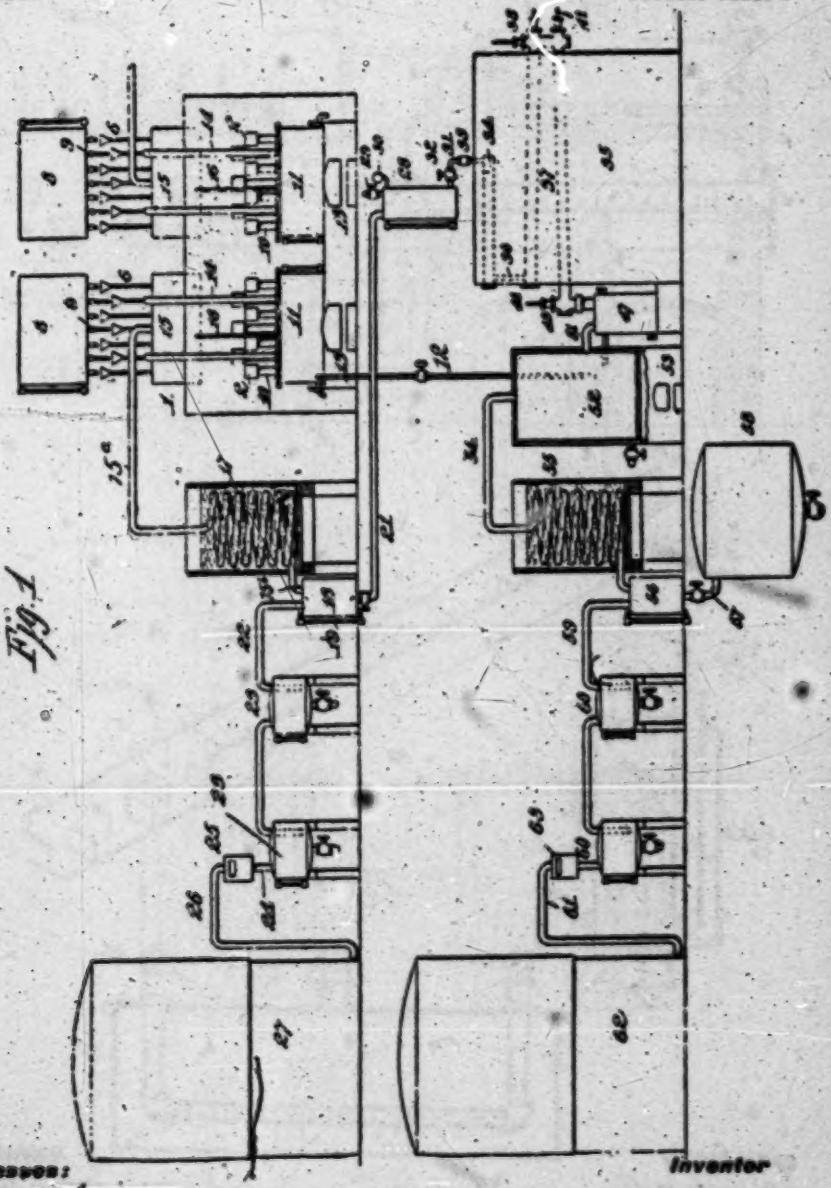

Fig. 1

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PX149-1

4388

[fol. 1108]

No. 755,309. PATENTED MAR. 22, 1904.

A. NIKIFOROFF.

MANUFACTURE OF THE BENZOLS AND THEIR HOMOLOGUES.

APPLICATION FILED SEPT. 8, 1902.

NO MODEL. 3 SHEETS—SHEET 2

Fig. 3

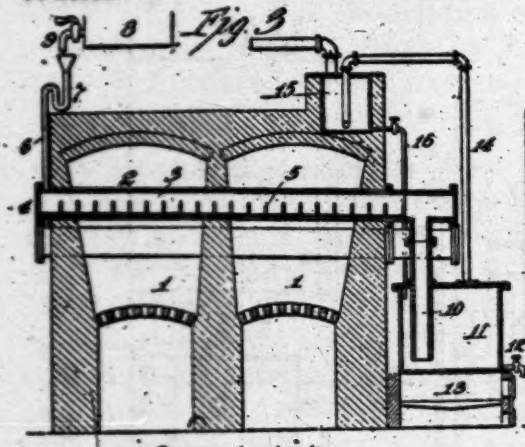

Fig. 2

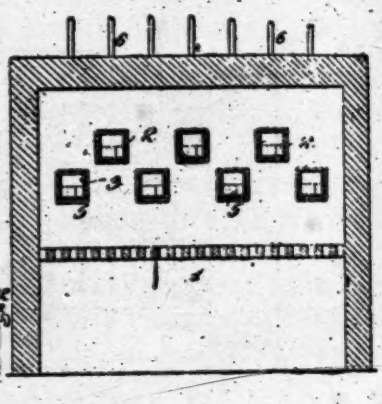

Fig. 4

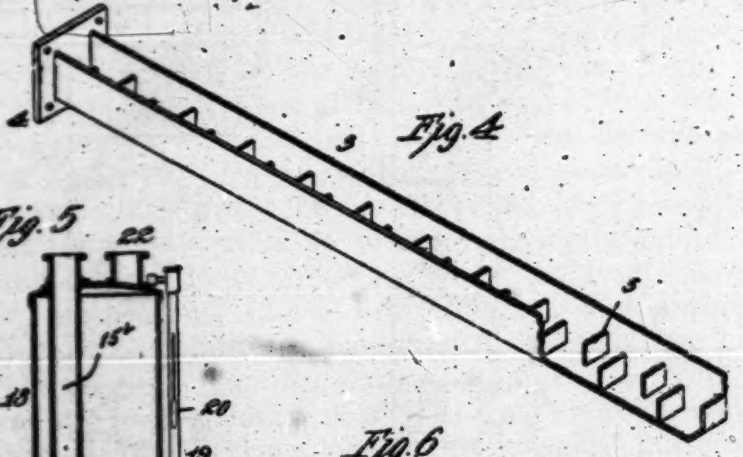

Fig. 5

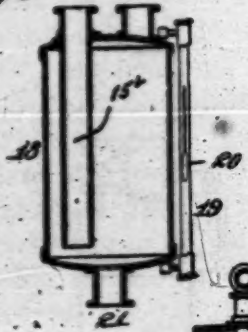

Fig. 6

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PX 149-24

[fol. 1109]

No. 755,309 PATENTED MAR. 22, 1904.

A. NIKIFOROFF.

MANUFACTURE OF THE BENZOLS AND THEIR HOMOLOGUES.

APPLICATION FILED SEPT. 6, 1902.

NO MODEL. 3 SHEETS—SHEET 3.

Fig. 7

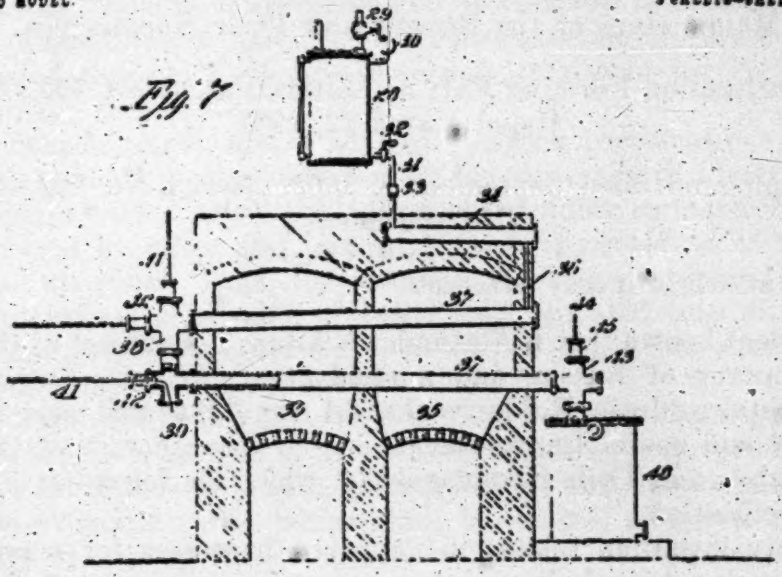


Fig. 8

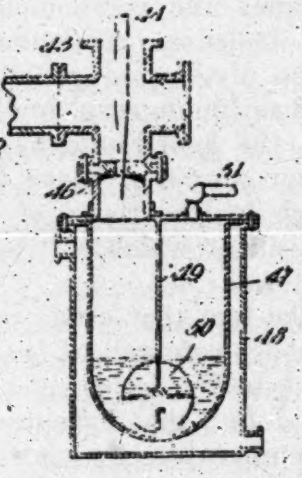


Fig. 9

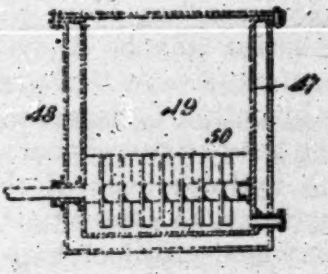
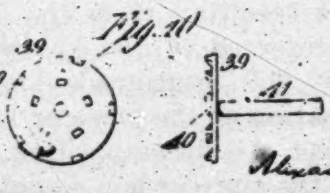


Fig. 10



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PX 149-3

[fol. 1110] No. 755,309. Patented March 22, 1904

United States Patent Office

Alexander Nikiforoff, of Moscow, Russia

Manufacture of the Benzols and Their Homologues

Specification Forming Part of Letters Patent No. 755,309, Dated March 22, 1904

Application filed September 8, 1902. Serial No. 122,531. (No specimens.)

To all whom it may concern:

Be it known that I, Alexander Nikiforoff, a subject of the Emperor of Russia, and a resident of Moscow, Russia, (postal address Rojdestvenka 8,) have invented certain new and useful Improvements in the Manufacture of the Benzols and Their Homologues, of which the following is a specification.

My invention relates to improved processes for manufacturing benzol, its homologues and compounds of the aromatic series from crude petroleum, petroleum residue, heavy oils resulting from the distillation of bituminous coal and the like, and from the residuum resulting from the manufacture of oil-gas—i. e., the final liquid by-products or tailings, including any other source of heavy liquid or solid hydrocarbon from which hydrocarbons of the aromatic series may be derived, all of which will be hereinafter referred to as "raw material."

My invention is based on the fact that crude petroleum and the heavy hydrocarbons above referred to, besides containing hydrocarbons of the paraffin series, also contain hexahydrocyclic compounds. I find that by subjecting to the combined effect of high temperature and pressure the volatilized products resulting from the decomposition of the raw materials referred to and having a boiling-point below approximately 200° centigrade I am enabled to effect the dehydrogenation of the more or less simple hydrocarbons and to effect the decomposition with subsequent dehydrogenation of the more or less complex hydrocarbons, resulting in the formation of benzol and of a whole series

of its derivatives, such as toluol, xylol, cumol, naphthalene, anthracene, &c. In this way I am enabled to carry my process into effect expeditiously and economically and when the original raw material is free from sulfur the resulting benzol obtained is entirely free from thiophene, the presence of which is unavoidable and detrimental in connection with benzol as obtained by other processes heretofore suggested and which requires elaborate treatment for its removal.

Benzol, toluol, and other hydrocarbon combinations of the aromatic series obtained by my process are identical in their useful properties with corresponding combinations secured by other and less advantageous processes at the present time. Thus, for instance, the benzol obtained by my process is capable of being fully nitrated into nitrobenzol, while the anthracene can be converted into alizarin with perfect dyeing properties.

My object generally is to provide a new and useful process for the treatment of heavy hydrocarbons for the production therefrom of benzol, its homologues and compounds of the aromatic series which shall be simple, effective, and capable of operation under conditions of the highest economy.

Broadly stated, my improved process consists, first, in subjecting the heavy hydrocarbon to decomposition, whereby the products vaporizing substantially below 200° centigrade are removed, so that at the very commencement of the operation I provide a product capable of being effectively operated upon by the subsequent treatments and eliminate the heavy tarry residuums, which would otherwise clog the apparatus and retard the operations; second, in subjecting the distillate thus secured, volatilizing substantially below 200° centigrade, to the effect of high temperature under a pressure above the atmospheric, whereby some of the hydrocarbons are dehydrogenated, while the complex hydrocarbons are first decomposed and subsequently dehydrogenated, and in separately recovering the aromatic distillate thus secured, and, third, in subjecting the separate aromatic distillates obtained as explained, if necessary, to the effect of fractional distillation or other treatment in any well-known way for the recovery of benzol or any of its derivative aromatic compounds, all as will be more fully hereinafter described and claimed.

In order that the invention may be better understood, attention is directed to the accompanying drawings, forming part of this specification, in which——

Figure 1 is a diagrammatic view illustrating a suitable apparatus for carrying the process into effect; Fig. 2, a transverse sectional view of the retort-furnace for subjecting the raw material to a preliminary decomposition; Fig. 3, a longitudinal sectional view of the same through one [fol. 1111] of the retorts; Fig. 4, a separate sectional perspective of one of the troughs employed in each of the decomposition-retorts; Fig. 5, a sectional view of the tank for receiving the useful distillate secured in the preliminary decomposition operation; Fig. 6, a view, partly in section, of the separating-tank employed for separating the useful distillate from the products of distillation or decomposition obtained in the first decomposition, and whose boiling-point is approximately above 200° centigrade and below 250° centigrade; Fig. 7, a separate sectional view through the retort in which the second operation is performed for subjecting the useful distillate of the first decomposition to the combined effect of high temperature and pressure; Fig. 8, a separate sectional view illustrating the wash-tank for washing the distillate of the second operation and showing also the needle-valve for regulating the pressure in the high-temperature retorts; Fig. 9, a longitudinal sectional view of the wash-tank, and Fig. 10 detail views illustrating the preferred form of scraper for removing sediment from the high-temperature retorts.

In all of the above views corresponding parts are represented by the same numerals of reference.

The decomposition-furnace comprises the furnaces 11 and a plurality of inclined retorts 2, made, preferably, of cast-iron. Within each retort is a removable trough 3, whose flange 4 forms one end of the retort and is bolted in place. Each of these troughs is provided with staggered baffle-plates 5, so that the hydrocarbon in flowing down the same will be caused to take a tortous course. When the troughs become objectionably clogged with the heavy residuum resulting from the first decomposition, they may be removed and cleaned, as will be understood. The several decomposition-retorts 2 are supplied with raw material through feeding-pipes 6, having traps 7 to form a seal. These feeding-troughs receive material from a tank 8, hav-

ing a plurality of valved nozzles 9 corresponding with the several feeding-pipes. A discharge-pipe 10 leads from each decomposition-retort and extends into a tank 11, having a valved draw-off pipe 12 and heated in any suitable way, as by a furnace 13, so that its temperature shall be approximately 250° centigrade. It is to be understood that this furnace is used only in beginning operations. Afterward its use will not be necessary. Leading from the tank 11 is a vapor-pipe 14, entering a separator 15 and equipped at its lower end with a perforated extension (see Fig. 6) located close to the bottom of the separator, as shown. The separator 15 is arranged above the retort-furnace, and its temperature is maintained at from 175° to 200° centigrade by the heat of the furnace or in any other way. A valved pipe 16 connects the bottom of the separator 15 with the tank 11, as shown. A vapor-pipe 15^a leads from the top of the separator 15 to condenser 17 and thence, as indicated at 15^b, to a receiving-tank 18, provided a glass gage 19, having a hydrometer 20 therein, by means of which the specific gravity of the distillate deposited in the receiving-tank 18 can be observed at any time. Leading out of the bottom of the receiving-tank 18 is a valved draw-off pipe 21, and out of the top of that tank is a vapor-pipe 22, connected with a series of solvent-tanks 23, as shown, supplied with any suitable solvent, such as acetone or methylic alcohol. From the final solvent-tank a vapor-pipe 24 leads to a gas-meter 25, by which the volume of substantially permanent gas leaving the solvent-tanks may be measured. A vapor-pipe 26 conveys the uncondensed vapors to a gas-holder 27 of any suitable construction.

The valved draw-off pipe 21 from the receiving tank 18 leads to a supplying-tank 28 for furnishing to the high-temperature retorts the distillate useful for the production of hydrocarbons of the benzol series. This supply-tank is furnished with compressed air, compressed carbonic-acid gas, or other neutral gas through a valved pressure-pipe 29, and the pressure is indicated on a gage 30. Leading from the supply-tank 28 at its bottom is a pipe 31, furnished with a cut-off valve 32 and with a check-valve 33, the latter permitting the liquid to flow out of the supply-tank, but preventing a flow of the liquid in the opposite direction. The pipe 31 leads to a supplemental retort 34 in the top of the furnaces 35 and by means of which the useful

distillate will be vaporized, so as to be supplied to the high-temperature retorts in a vaporized condition, whereby I am enabled to obtain a more intense and uniform decomposition in the latter retorts.

From the auxiliary retort 34 a pipe 36 leads to the high-temperature retorts 37, connected together in series, in order that the vapors may be subjected to the effect of high temperature and pressure for a relatively prolonged period. The retorts 37 are connected by a pair of four-way castings 38, as shown, in which are mounted a plurality of scrapers 39, (see Fig. 11,) having teeth 40 and carried on rods 41 passing through stuffing-boxes 42. By operating these scrapers I provide for the effective cleaning of the high-temperature retorts as well as the connections between the same, as will be understood. A door 38ª at the bottom of the casting allows of its being cleansed. The discharge end of the lowermost retort 37 is furnished with a four-way casting 43, in the vertical passage of which is mounted a needle-valve 44, passing through a stuffing-box 45. The tapered lower end of this needle-valve coöperates with the tapered opening in a disk 46, so that by moving the needle-valve more or less within the opening the diameter of the latter may be regulated to thereby provide for the desired [fol. 1112] retardation of the flow of the products of decomposition through the same, with a consequent regulation of the pressure within the high-temperature retorts. Connected with the discharge from the high-temperature retorts is a washer (see Fig 8) comprising a receptacle 47, having a curved bottom, as shown, and contained in a water jacket 48, by which the receptacle may be always kept cool. Arranged within the receptacle 47 is a central vertical partition 49, dividing the same into two chambers, and below this partition is an agitator 50 of any suitable construction, the shaft of which is rotated from any desired source of power. From the washer a vapor-pipe 51 leads to a tank or vessel 52 for containing naphthalene-oil and anthracene-oil and which is heated in any suitable way—as, for example, by a furnace 53 beneath it—so that its temperature shall be approximately from 200° to 225° centigrade. A vapor-pipe 54 leads from the top of the vessel 52 to a condenser 55 and thence to a receiving tank or vessel 56, preferably corresponding in construction with the tank 18 and which therefore does not require detailed illustration. A valved

draw-off pipe 57 leads from the bottom of the tank 56 to a receiving vessel 58 for receiving the aromatic distillate. Leading from the top of the vessel 56 is a vapor-pipe 59, connected with a series of solvent-tanks 60, supplied with a suitable solvent, such as acetone or methylic alcohol, and leading from the final solvent-tank of the series is a vapor-pipe 61, supplied with a gas-meter 63 and connected to a suitable gas-holder 62.

In the carrying out of my improved process for the treatment of any suitable raw material—such, for example, as crude Balakhani petroleum—I proceed substantially as follows: The crude material is supplied to the tank 8 and from the latter fed to the several decomposition-retorts 2 through the supply-pipes 6. In flowing through the troughs 3 the passage of the liquid material is obstructed by the baffle-plates 5, so that it partakes of a tortuous course, and consequently is subjected to the effect of the heat for a relatively prolonged period. In these decomposition-retorts the crude material is subjected to a temperature of from 500° to 525° centigrade, and the material will be thus evaporated and partly decomposed. The volatile products of the decomposition or evaporation pass through the vapor-pipe 10 into the tank 11, which is maintained at a temperature of approximately 250° centigrade. Any vaporized products volatilizing at a temperature above 250° centigrade will thereby condense and accumulate in the tank 11, from which they may be withdrawn from time to time as desired. The liquid collected in tank 11 corresponds in its character to the residuum obtained in the distillate of crude kerosene-oil, and its use, beyond the small portion employed for charging the washer 47, is for fuel or for the manufacture of lubricating-oil. The vapors having a boiling-point below 250° centigrade pass through the vapor-pipe 14 and enter the separating-tank 15, maintained at a temperature of from 175° to 200° centigrade. In this separating-tank I condense the vapors whose boiling-point is 200° centigrade or more. The more volatile vapors, boiling below approximately 200° centigrade, pass through the vapor-pipe, and their condensable portion is condensed by the condenser 17 and accumulates in the receiving-tank 18. Any non-condensable gases will be conducted through the several solvent-tanks 23 and their soluble constituents removed by the solvent therein. The solution thus secured

can be subjected to any desired distilling process for the separation of the solvent from the dissolved hydrocarbon. The hydrocarbon recovered from the solvent-tanks volatile parts of useful distillate—i. e., principally a small quantity of benzol—resulting already at this period of the decomposition. From the solvent-tanks 23 the permanent gas passes through the gas-meter 25, by which its volume is measured, and enters the gas-holder 27, from which it may be removed for use. The gas obtained in this manner is a final product, and in the example given with Balakhani petroleum will amount to about 12.85 per cent of the amount of material used and finds ready use for heating, lighting, and other industrial purposes.

I find in practice that in the tank 15 is collected and condensed a small proportion of distillate vaporizing under a temperature of 200° centigrade and having useful properties in this art. This residuum consists of a mixture of a material somewhat similar to the residuum as in tank 11, with a portion of the condensed vapors which in the course of operation condense before reaching the condenser 17. In order that these volatile products can be recovered, it is only necessary to withdraw the contents of the tank 15 into the vessel 11 through the valved pipe 16, (see Fig. 3,) whereby the relatively high temperature of the latter (250° centigrade) will again evaporate and distillate and carry it over into the tank 15. This may be done from time to time as most convenient to the operator.

The troughs 3 after a few hours of continued use accumulate porous coke, and in order that this may be removed the several troughs are withdrawn, preferably one at a time, and are replaced by fresh troughs. By removing the troughs one at a time, as explained, I am enabled to operate the apparatus continuously.

I find in practice that by maintaining an approximately constant temperature in the retort-furnaces I am enabled to keep the process of decomposition under perfect control by merely adjusting the supply of raw material to the retorts in such a way as to keep the specific gravity of the [fol. 1113] condensed distillate in the tank 18 and the quantity of gas measured by the meter 25 approximately constant, so that in this way the process of decomposition is an extremely simple one.

The useful condensed distillate from the first decomposition collected in the receiving vessel 18 and which amounts in the given example to about fifty per cent of the entire amount of petroleum operated on is now subjected to the second operation of the process—namely, to the effect of high temperature under a pressure above atmospheric in the high-temperature retorts. It will be noted that by subjecting the raw material to a preliminary decomposition I obtain in the first instance a useful distillate capable of being acted upon directly for the production of benzol, its homologues, and compounds of the aromatic series and have eliminated the heavier residual hydrocarbons, which would otherwise not only clog the subsequent apparatus, but would unduly overload the same. Heretofore, so far as I am aware, in all attempts which have been made to obtain benzol, &c., from crude petroleum the entire bulk of raw material has been subjected to a decomposing operation, necessitating the use of retorts charged with refractory materials, such as coal, coke, iron, pumice-stone, and the like. These retorts have become quickly clogged, so that the previous experiments have been slow and generally impractical. Thus the expedient of subjecting the raw material to a preliminary decomposition, although simple, is from the standpoint of utility highly important. The valve in the draw-off pipe 21 is now opened and a charge from the tank 18 enters the supply-tank 28. The valve is now closed and pressure is admitted to the supply-tank through the pressure-pipe 29, so that when the valve 32 is opened material from the supply-tank will be forced into the high-temperature retorts. The temperature maintained in the retorts 37 varies from 900° to 1,000° centigrade, and the temperature maintained in the auxiliary retort 34 is obviously somewhat lower, but is always sufficient to effect a vaporization of the liquid hydrocarbon. Consequently the liquid hydrocarbon entering the auxiliary retort 34 will be vaporized, so that it enters the high-temperature retorts 37 in a vaporized condition, whereby I am enabled to obtain a more intense and uniform decomposition in the latter. The subjection of the vapor in the retorts 37 to high temperature results in the generation of a pressure which can be regulated by the needle-valve 41, as explained. In the example given a pressure of about fifteen pounds above at-

mospheric is maintained. Should this pressure ever overbalance the pressure in the tank 28, the check-valve 33 will be closed, so as to automatically protect the supply-tank 28 from the effect of any accidental excessive pressure which might take place—for example, if the tapered opening in the disk 46 became clogged. This opening can, however, be ordinarily kept perfectly free by means of the needle-valve 44.

The gases and vaporized products of decomposition leaving the high-temperature retorts are conducted to the washer 47, which is supplied with the residuum from the first decomposition drawn from the tank 11 through the pipe 12 or any other distillate boiling above 250° centigrade obtained by any process to just submerge the lower end of the partition 49, and thereby form a seal between the two chambers. In this washer the products of decomposition are cleaned of any particles of fine soot which may become mechanically entrained therewith. From the washer the vaporized products of decomposition are conducted to the tank 52, maintained at a temperature of from 200° centigrade to 225° centigrade and in which the materials condensing at that temperature are collected, principally and essentially anthracene oil and naphthalene oil. The condensable vapors whose boiling-point is below approximately 200° centigrade are condensed by the cooler 55 and accumulate in the tank 56, from which they may be removed and accumulated in the tank 58. This condensed distillate I refer to as the "aromatic" distillate and in the example given amounts to about 21.50 per cent of the original material. The uncondensed vapors from the tank 56 pass through the solvent-tanks 60 and any soluble constituents are removed therefrom, the substantially permanent gas passing through the gas-meter 63 to the gas-holder 62, from which it may be used when desired. The gas thus obtained in the example given is about 16.15 per cent of the original material, is a final product, and may be used for the same purposes as the gas obtained with the holder 27, either alone or mixed with the gas obtained by the first decomposition.

As a result of the process of decomposition described effected at high temperature and under a pressure above atmospheric I secure products which can be subjected to any desired subsequent treatment for the obtaining of useful

hydrocarbons by any of the well-known processes. For instance, the products condensed in the tank 52, having a boiling-point above approximately 200° or 225° centigrade, can be subjected to any well-known process for obtaining naphthalene or anthracene, the aromatic distillate received in the tank 58 can be subjected to fractional distillation in well-known ways to obtain benzol and its immediate derivatives, while the solution in the solvent-tanks 60 can be diluted with water and regenerated, if acetone or methylic alcohol is used as absorbents, for the recovery of aromatic distillate. If absorbents are used which are not soluble in water, the solution can be subjected to fractional distillation. The [fol. 1114] aromatic distillate, either alone or in addition to the product in the tank 58, can be subjected to fractional distillation for further refinement.

In the example given—viz., operating upon Balakhani petroleum—the following percentages of the original amount have been obtained: 8.12 per cent of ninety per cent commercial benzol, 2.51 per cent of commercial tuluol, and 1.20 per cent of xylol.

The following diagram indicates in schematical form a general outline of the entire process:

Example of Process Applied to Balakhani (Caucasian) Petroleum

Crude petroleum is subjected to decomposition at about 500° centigrade and produces—

- Gas about 12.85 per cent.
- "Useful oil," which has a boiling-point of below 200° centigrade, about fifty per cent., which is subjected to decomposition at a temperature of about 900° centigrade and under a pressure of about fifteen pounds above atmospheric, producing—
  - Gas about 16.15 per cent. of original petroleum.
  - "Aromatic distillate" about 21.50 per cent. of original petroleum, which is subjected to fractional distillation in the usual manner, and produces—
    - Ninety per cent. commercial benzol about 8.12 per cent. of original petroleum.
    - Commercial tuluol about 2.51 per cent. of original petroleum.
    - Xylol about 1.20 per cent. of original petroleum.
  - Residuum and waste about 12.35 per cent. of original petroleum.
- Residuum, coke, and waste about 37.15 per cent.
  - Residuum 9.67 per cent. of original petroleum.

it is to be understood that when my improved process is used in connection with other petroleums, or when other petroleums and other substances, such as petroleum residue, heavy oils resulting from the distillation of bituminous coal, and the like—are used as raw materials the temperatures and pressures will be varied, as determined by experiment.

As I have described my process as applied to crude Balakhani petroleum with a temperature at the first operation of about 500° centigrade and the second operation of about 900° centigrade under a pressure of about fifteen pounds above atmospheric, I desire it understood that such temperature and pressure are cited merely as an example. I believe that my process may be successfully applied to some substances by employing a temperature in the second operation of as low as 750° centigrade and that the pressure can be varied within very wide limits.

It will be understood that if my improved process is to be used in connection with the decomposition of solid hydrocarbons the latter may be first fused and then admixed with a sufficient quantity of raw material, as defined above, to constitute a viscous liquid capable of flowing through the decomposition-retorts.

The apparatus described in the specification is not claimed herein but forms the subject-matter of an application for patent filed January 14, 1903, Serial No. 139,024.

Having now described my invention, what I claim as new, and desire to secure by Letters Patent, is—

1. The process of treating raw materials, substantially as set forth, for the production of an aromatic distillate capable of yielding benzol, which consists in subjecting the raw material to a preliminary decomposition to separate hydrocarbons having a boiling-point of approximately 200° centigrade or under, and in then subjecting the distillate so secured to the effect of a temperature of about 750° centigrade and under a pressure above the atmosphere, as and for the purposes described.

2. The process of treating raw materials, substantially as set forth, for the production of an aromatic distillate capable of yielding benzol, which consists in subjecting the raw material to the effect of decomposition under a temperature

of approximately 500° centigrade, in collecting the vaporized distillate having a boiling-point of approximately 200° centigrade or under, and in subjecting such distillate to the effect of a temperature of about 750° centigrade under a pressure above the atmosphere, as and for the purposes described.

3. The process of treating raw materials, substantially as set forth, for the production of an aromatic distillate capable of yielding benzol which consists of decomposing the raw material under the effect of heat, in condensing the volatile distillate having a boiling-point 200° centigrade or under, and in subjecting such distillate to the effect of a temperature of about 750° centigrade under a pressure above that of the atmosphere, in collecting the distillate of the second decomposition whose boiling-point is approximately 200° centigrade or over, and in separately collecting the aromatic distillate of the second decomposition whose boiling-point is 200° centigrade or under, as and for the purposes set forth.

4. The process of treating raw materials, substantially as set forth, for the production of an aromatic distillate capable of yielding benzol, which consists in decomposing the raw material under the effect of heat, in condensing the volatile distillate having a boiling-point of 200° centigrade or under, in subjecting such distillate to the effect of a temperature of above 750° centigrade under a pressure above that of the atmosphere, in collecting the distillate of the second decomposition whose boiling-point is approximately 200° centigrade or over, in separately collecting the aromatic distillate of the second decomposition whose boiling-point is 200° centigrade or under, and in subjecting the uncondensed vapor of the second decomposition to the effect of a solvent, as and for the purposes set forth.

[fol. 1115] 5. The process of treating raw materials substantially as set forth, for the production of an aromatic distillate capable of yielding benzol, which consists in decomposing the raw material under the effect of heat, in condensing the volatile distillate having a boiling-point of 200° centigrade or under, is subjecting such distillate to the effect of a temperature of above 750° centigrade under a

pressure above that of the atmosphere in collecting the distillate of the second decomposition whose boiling-point is approximately 200° centigrade or over, in separately collecting the aromatic distillate of the second decomposition whose boiling-point is 200° centigrade or under, in subjecting the uncondensed vapor of the second decomposition to the effect of a solvent, and in finally collecting the uncondensed permanent gas, as and for the purposes set forth.

6. The process of treating a hydrocarbon derived from raw material, substantially as set forth, and whose boiling-point is 200° centigrade or less, which consists in subjecting such hydrocarbon to the effect of a temperature of about 750° centigrade under a pressure above atmospheric, and in subsequently condensing and collecting the aromatic distillate, as and for the purposes set forth.

7. The process of treating a hydrocarbon derived from raw material, substantially as set forth, and whose boiling-point is 200° centigrade or less, which consists in subjecting such hydrocarbon to the effect of a temperature of above 750° centigrade under a pressure above that of the atmosphere, in collecting and condensing the aromatic distillate, and in passing the uncondensed distillate through a solvent, as and for the purposes set forth.

8. The process of treating a hydrocarbon derived from raw material, substantially as set forth, and whose boiling-point is 200° centigrade or less, which consists in subjecting such hydrocarbon to the effect of a temperature of above 750° centigrade under a pressure above that of the atmosphere, in collecting and condensing the aromatic distillate, in passing the uncondensed distillate through a solvent, and in subsequently collecting the permanent gas, as and for the purposes set forth.

9. The process of treating a hydrocarbon derived from raw material, substantially as set forth, and whose boiling-point is 200° centigrade or less, which consists in subjecting such hydrocarbon to the effect of a temperature of above 750° centigrade under a pressure above that of the atmosphere, in collecting and condensing the vaporized distillate whose boiling-point is above 200° centigrade, and in separately condensing the aromatic distillate whose boiling-

point is above 200° centigrade, as and for the purposes set forth.

10. The process of obtaining benzol from raw materials, substantialy as set forth, which consists in subjecting the raw material to the effect of high heat, in condensing the distillate having a boiling-point of 200° centigrade or less, in subjecting such distillate to the effect of a temperature above 750° centigrade under a pressure above that of the atmosphere, in condensing the aromatic distillate derived from the second decomposition, and in fractionally distilling the aromatic distillate so obtained, as and for the purposes set forth.

11. A step in the process of obtaining benzol from a hydrocarbon whose boiling-point is 200° centigrade or less, derived from the decomposition of crude materials, substantially as set forth, which consists in subjecting the hydrocarbon to the effect of a temperature above 750° centigrade under a pressure above that of the atmosphere, in collecting and condensing the aromatic distillate, and in fractionally distilling such distillate, as and for the purposes set forth.

12. A step in the process of treating raw materials, substantially as set forth, preparatory to the decomposition thereof for the production of an aromatic distillate from which benzol can be immediately derived, which consists in subjecting a current of the raw material to contact with a surface heated to 500° centigrade whereby the material is gradually raised in temperature, and in collecting the products of decomposition thus obtained and separating those whose boiling-point is approximately 200° centigrade or less, from those whose boiling-point is above 200° centigrade, as and for the purposes set forth.

In witness whereof I have hereunto set my hand in presence of two witnesses.

Alexander Nikiforoff. [L. S.]

Witnesses: Nausu Mintz, Stefan von Otteretzky.

4404

[fol. 1116]

(No Model.)

PETITIONER'S EXHIBIT 150

G. L. BENTON.

PROCESS OF REFINING CRUDE PETROLEUM OIL.

No. 342,564. Patented May 25, 1886.

Fig. 1

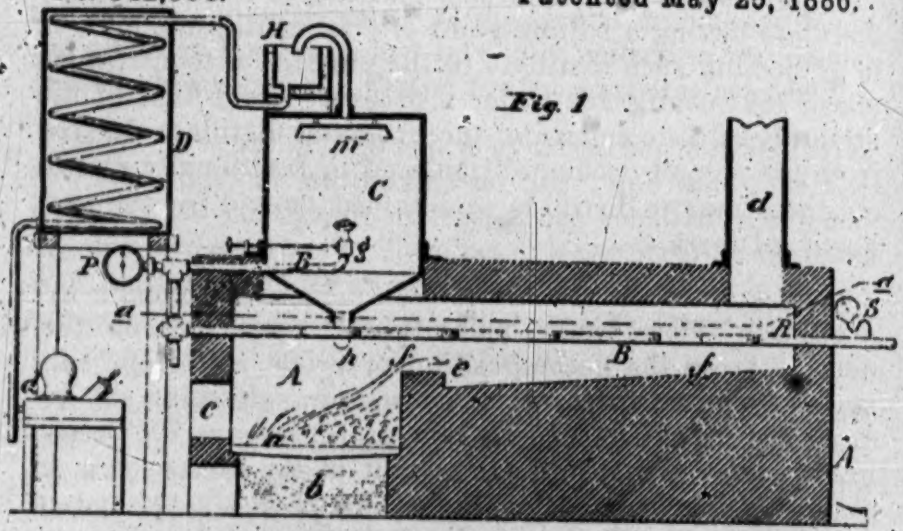


Fig. 2

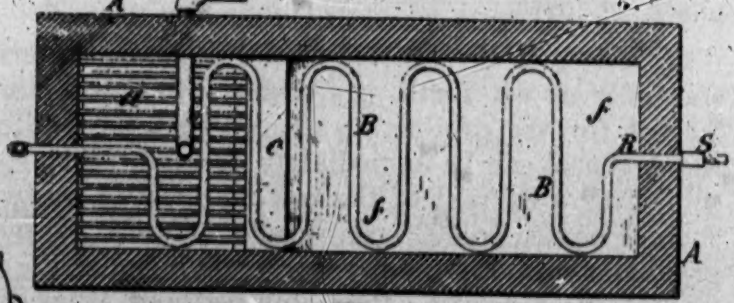
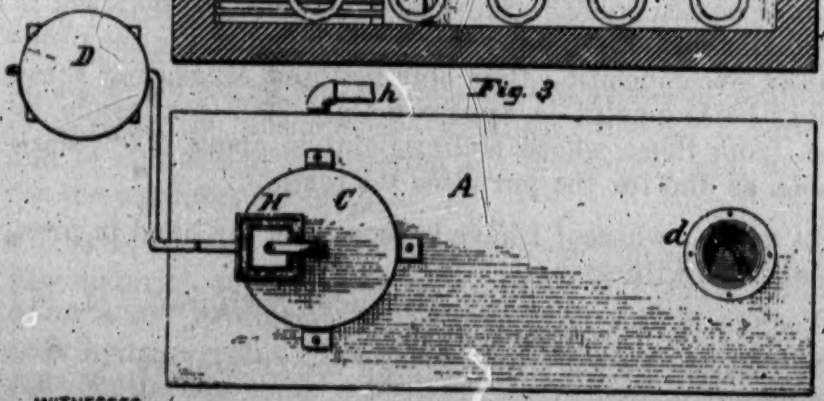


Fig. 3



WITNESSES:

C. A. Woodruff Jr.

C. A. Woodruff.

INVENTOR

George L. Benton

By Gillette Hopkins

Atty

PX150-1

[fol. 1117] United States Patent Office

George L. Benton, of Titusville, Pennsylvania

Process of Refining Crude Petroleum-Oil

Specification Forming Part of Letters Patent No. 342,564, Dated May 25, 1886

Application Filed February 25, 1885. Serial No. 156,993. (No model)

To all whom it may concern:

Be it known that I, George L. Benton, of Titusville, in the county of Crawford and State of Pennsylvania, have invented certain new and useful Improvements in Processes of Refining Crude Petroleum, of which improvements the following is a specification.

My invention relates to an improved method of refining crude petroleum that is extracted directly from the earth in contradistinction to that which has undergone the usual primary distillation before refinement.

The object of my invention is to confine the crude petroleum under high heat and pressure so as to cause a thorough chemical union or combination of the different homologous hydrocarbons comprising the same, so that when allowed to expand under a uniform temperature these different hydrocarbons or the component parts of the petroleum will vaporize simultaneously, forming a homogeneous vapor and containing in its bulk the benzine which has heretofore ordinarily been expelled therefrom and utilized for other than illuminating purposes, and this vapor, when condensed, producing a homogeneous illuminating-oil, such as hereinafter more particularly explained.

Crude petroleum is chemically defined as "consisting almost entirely of a mixture of homologous hydrocarbons," these hydrocarbons having different specific gravities, and when such petroleum is refined to a certain degree it is called "burning" or "illuminating" oil. This refined petroleum is still a compound of hydrocarbons having different specific gravities, and, this degree of refining being effected by treating the crude oil in stills or apparatus of

similar character, the petroleum of commerce is generally designated as a "distillate."

The refining of petroleum as ordinarily conducted is simply a fractional distillation by heat gradually increased at each stage, and the first product is what is designated as "benzine," which, while rich in illuminating properties, is too volatile to be so used with safety, and is therefore sold for other applications and at a less price than the heavier distillates. The benzine as it is driven off from the main body of the oil is condensed in the condensing chamber, and thence conducted to a separate tank, while the remainder of the oil is subjected to further continuous heat until another and heavier class of the hydrocarbon compounds is vaporized and likewise condensed and conducted to a separate chamber, this second product of the distillation being known as "illuminating-oils," and the residuum which is of too great specific gravity for such purposes, and which includes paraffine and other substances, all comprised technically under the designation of "tar," is then drawn off and utilized in various ways after treatment by different processes.

While the proportion of benzine varies in crude petroleum it is always considerable, and in some cases reaches as high as twelve per cent., so that it occasions a serious loss of the raw material used to have the benzine unavailable for illuminating purposes, and its value reduced, as already mentioned, and it is one of the objects of my invention to avoid this loss, and thereby increase the quantity and improve the quality of the illuminating-oil produced from a given quantity of crude material.

My invention consists, essentially, in subjecting the crude petroleum to high heat and pressure in a chamber or pipe or vessel, and so regulating the heat applied as to raise the temperature of the crude liquid to about 700° Fahrenheit or higher while maintaining a pressure of about five hundred pounds per square inch, more or less. Under this pressure the liberation of any vapor from the highly-heated crude liquid is prevented until the heat shall have been continued long enough and raised high enough to bring the entire body of the oil confined in the chamber or pipe or vessel to a uniform temperature, when it is next discharged in a spray into a vapor-chamber, in which the previous high

temperature is still maintained, but the pressure removed. The different hydrocarbons will vaporize simultaneously, forming a homogeneous vapor, (instead of first vaporizing the benzine, and then the next heaviest hydrocarbons, as heretofore mentioned,) and these liberated vapors will be kept homogeneous by the intimate chemical affinity of their constituents, while any unvaporizing portions of the mass accumulating precipitate in this intermediate vessel, from the bottom of which they may be drawn off through a suitable pipe and cock. The final step consists in conducting [fol. 1118] the homogeneous vapors from this vapor-chamber to an ordinary condenser, which may consist of a coil if pipes immersed in water in a tank or other containing vessel, and this condensation reduces the vapor to a homogeneous fluid possessing all the most desirable properties of high-test illuminating oil, and containing in its homogeneous bulk substantially all of the benzine, which has heretofore ordinarily been expelled from it, as previously mentioned.

In the accompaning drawings I have represented an apparatus such as I have used with practical success in the conduct of my improved process.

Figure 1 is a vertical longitudinal section through the apparatus. Fig. 2 is a horizontal longitudinal section on the line of *a a* of Fig. 1, and Fig. 3 is a plan or top view.

This apparatus consists of a furnace, A, constructed of brick-work, and provided with a grate, *a*, an ash-pit, *b*, a door, *c*, a chimney, *d*, a fire-bridge, *e*, and a chamber space, *f*, extending from end to end and from side to side of the interior of the furnace, as seen in Figs. 1 and 2.

In the chamber-space *f* is arranged the coiled pipe B, Fig. 2, connected at the rear end through the furnace-wall with the oil-supply, and provided at this end with a pressure-gage, S, and an overflow pressure valve, *q*, of any suitable construction to prevent undue increase of pressure in the pipe B. This pipe extends at the front end through the furnace-wall, and is provided with a pyrometer, P. The pipe B is continued up into the vapor-chamber C, as shown, and this end of the pipe B is provided with a rose or perforated cap, through which the highly-heated crude oil can be sprayed into the chamber C. I prefer to connect with the pipe B, outside of the furnace, a waste-pipe *i*, with a stop-cock, *k*, for a purpose to be presently described.

The vapor-chamber C is an inclosed metallic vessel of suitable strength and made air-tight. It is fitted into the top of the furnace, as shown, and has a dished bottom, which is exposed to the heat of the furnace or chamber *f*, and it has an outlet-pipe, *h*, leading off through the furnace to the outside. Underneath the top of this vapor-chamber C, and above the spray-pipe B, is a deflecting-hood, *m*, extending out toward the sides of the chamber, but having an annular space between the edge of the hood and the side of the vapor-chamber. In the top of the vapor-chamber is a pipe which leads off preferably to the manifold H, which is a condensing-box of the ordinary construction, and thence by pipes to the condenser D, or the vapor may pass directly from the chamber C to the condenser D; and at the lower end of this condenser an air-pump may be attached, as shown in the drawings, and for a purpose to be hereinafter specified. A stop-cock, *g*, is so arranged as to be operated from the outside of the vapor-chamber, and to be opened or shut, as it is desired, to regulate the discharge of the highly heated oil from the pipe B into the chamber C, or to confine it to the pipe B.

In this apparatus the operation is conducted as follows: The stop cock *g* being shut and the waste-pipe *i*, connected with the pipe B, being opened, a fire is started on the grate *a*, and the crude oil is let in from the supply to the coil-pipe B and allowed to flow out through the waste-pipe *i*, (from which it is led back to the supply,) while the pipe B and the chamber *f* attain the proper temperature, which will be ascertained by the observation of the workman in charge. When he finds that the furnace has attained the proper temperature, he shuts the waste cock *k*, and the stop-cock *g* being already shut thus confines the oil in the pipe B under the pressure of the supply or of a pump, T, which feeds the oil to the pipes. The oil with which the pipe B is thus filled is kept in the pipe under this pressure until the pyrometer indicates that it has attained a temperature sufficiently high to have had the latent vaporizing effect upon the oil, (in practice I have found this temperature to range from 700° to 1,000° Fahrenheit), when the stop-cock *g* is opened and the released vaporized oil rushes out through the rose in the end of pipe B and strikes on the under side of the hood *m*, from which it is deflected downward, and then rises

through the annualar space between the hood and the wall of the chamber C, and passes into the pipe which leads directly to the condenser D or to the manifold H, and thence by pipes to the condenser D, and through this condenser into a receiving-tank of any ordinary construction. It will be understood that the chamber C will have become heated before the admission of the vaporized oil into it, and that its temperature is maintained by the furnace to correspond substantially with that of the spray escaping into it from the coiled pipe B, through which the passage of the crude oil is now kept up continually under the regulated pressure at such velocity as to provide time for its required increase of temperature while passing through the furnace.

To promote the passage of the vapor from the chamber C to the condenser D, I connect an ordinary air-pump with the lower end of the coil D at *d'*, and thus facilitate the operation. By this process I have found that the oil is raised to and maintained at a sufficiently high temperature to vaporize it as soon as it is released from the pressure under which it is confined in the pipe B, while, until so released, it is prevented by the pressure from vaporizing at all, and, consequently, when it is permitted to escape into the heated chamber C it bursts into vapor, and this vapor is entirely homogeneous, so that, after being deflected in the chamber C and then rising again to pass off into the condenser D, it passes off into a homogeneous volume, while depositing in the bottom of the chamber C such heavy or non-volatilized [fol. 1119] impurities as may have been in the crude petroleum. These accumulating impurities are drawn off through the pipe *h* in the bottom of the chamber C.

My improved apparatus, such as I have hereinafter described and have used with practical success, in the conduct of this improved process, forms the subject-matter of a separate application for a patent (Serial No. 165,310) under date of May 13, 1885.

In the conduct of this improved process I do not confine myself to the degrees of high temperature, nor to the amount of high pressure hereinbefore mentioned, as both require to be changed, or their proportions relatively have to be varied to determine either the quality of the illuminating-oil to be made from a given quality of crude material

or the quantity of oil to be obtained from a given amount of crude petroleum.

I am aware that hydrocarbon oils have been subjected to the action of heat under pressure while in a state of transit, whereby the oil has been raised to a temperature ranging from 100° to 330° Fahrenheit, to cause the separation of the lighter gases from the heavier oils on the removal of the pressure, and I therefore do not wish to claim any such process; but,

What I do claim as my invention, and desire to secure by Letters Patent, is—

The process of refining crude petroleum, which consists in heating the oil to a temperature ranging from about 700° to 1,000° Fahrenheit, and under a pressure of about five hundred pounds, or more, to the square inch, then causing the heated oil to expand into a chamber of approximately the same temperature, and finally conducting it into an ordinary apparatus wherein it is condensed, substantially as described.

George L. Benton.

Witnesses: C. W. Burtis, J. L. Moetz.

[fol. 1120] Translation of Petitioner's Exhibit No. 151

(No. 37, 1895)

Petroleum Development from Fish-oil as a Lecture Experiment

By Dr. C. A. Lobry de Bruyn, Chemiker Zeitung, 1895, p. 855

The known experiments by Engler[s]) to develop petroleum, by pressure distillation from animal fats and sebacic acids; are to be regarded as an important foothold for the theory of the animalic origin of petroleum. From his experiments Engler used at times a special large apparatus, and again ordinary bent glass tubes that were heated in digestors for four hours or longer. The latter method can now simply be turned—into a lecture experiment of a duration of about a quarter—of an hour, if a process is followed

that is explained in the following sketch. The one end of the glass tube bent approximately rectangularly, and filled one third to one half with fish oil, is being inserted into a piece of broken non-too-wide gas pipe; the remaining space between the two pipes is filled with sand in a manner that the glass pipe does not touch the iron wall; following this, intense heating with a three-armed burner is started. In the exposed end water and a clear liquid, the petroleum will soon distill over. The lower watery layer, can be made visible in a large auditorium by pasting a small piece of water-blue on the glass wall prior to the bermetic sealing, which will dissolve in the water thus developed. In the heated end a brown residue will settle; no carbon development takes place. The tube can in a measure be regarded as a minature petroleum well; the three layers, water, petroleum, and the inflammable gases are present under pressure. If the quantity of fish-oil is no larger than mentioned, the inner pressure in the cooled off tube, judged by the volumes of the gases, can be estimated at about 15 at-[fol. 1121] mospheres. As is known, good non-too-wide tubes can withstand considerable pressure. The carrying out of the experiment is then not wrought with danger, furthermore, the unheated end of the tube can be placed into a wide tube of wire netting. If heating is accomplished prior to the lecture, the presence of the inflammable gases under pressure can be shown by the circumstances, that the liquid contents can already be ignited at normal temperature, which sufficiently proves the transformation of the fish oil. Moreover, by this experiment an odor, like acrolein is apparent, which develops in the beginning at least, prior to the actual pressure distillation. By a distillation of fish-oil under ordinary atmospheric pressure the development of acrolein is considerably greater.

[fol. 1122] Translation of Petitioner's Exhibit No. 152

Engler-Hofer—Das Erdol, Vol. 1, p. 120

Pressure is only necessary to prevent a too far going destruction of the molecule, since as we already know, fat substances, when heated under pressure of 1 Atm., sepa-

rate into very many gases and carbon with little oil, under pressure of 10-25 Atm. yield practically only hydrocarbon oils. High temperature, as maintained by the Engler experiments, must therefore not be accepted as the natural development of crude oil, moreover, the same process might take place under considerably lower temperature in an indefinite period. In any event, however, carbonization and gasification is prevented through the concurrence of pressure.

That by this violent decomposition,—wholly apart from the so-called migration of the crude oil—the products can be more or less widely segregated through distillation, and, that liquid products of decomposition can only change location through pressure or capillary effect of neighboring layers, let us call this "capillary distillation," and, finally, that the transformable products remain at the place of their development as was proven experimentally by Engler by the production of synthetic crude oil, through heating of fatty substances under pressure, without distillation, must here again be particularly mentioned.

[fol. 1123] PETITIONER'S EXHIBIT No. 153

The Journal of the American Chemical Society

Volume XV, 1893

Committee on Papers and Publications: Edward Hart, Editor; J. H. Long, Edgar F. Smith

Easton, Pa., Chemical Publishing Co. 1893. H

On the Artificial Production of Petroleum[1]

By Dr. C. Engler

Scientists have discussed very often in the last few years the question in which way petroleum, this source of wealth, with its special scientific interest for this country, was

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[1] Read before the World's Congress of Chemists, August 23, 1893.

formed by nature. According to one theory it is generated from inorganic materials. Sokoloff thinks, that petroleum was produced during the period of the formation of our planet out of cosmical hydrocarbons, which in the beginning dissolved in the soft mass, separated from it later on. Mendelejeff assumes that water entering by fissures and chasms the interior of the earth came in contact with melting carbide of iron and produced so in a simple manner oxide of iron and the hydrocarbons of petroleum. Strong objection cannot be made to these two theories from the chemical standpoint; but the composition of the different [fol. 1124] kinds of petroleum is against them, and geology considers them not free from objections.

For a series of years the idea that petroleum was produced from the remains of plants by a kind of a distillation process, was most generally adopted, especially by chemists. Chemical and geological reasons are against this theory. From the chemical standpoint it seems quite impossible that the substance of the plants could be split up by distillation into petroleum without leaving charcoal or coke. There would also be a genetic conenction between coal and petroleum; but in occurrences of the ordinary kind, coal is nearly always absent. If this were really the case, then there ought to be with every oil occurrence in close connection a coal bank, which really seldom happens.

By a third theory the remains of animals form the raw materials from which petroleum is formed in nature. There are many facts proving the decay of masses of animals which we find now in banks in the crust of the earth in the form of the remains of shells, fishes, saurians, etc. Prominent scientists, amongst them the Americans, Wrigley, Whitney, Hunt, and others, and in Europe Höfer and Ochsenius especially, defend this idea on geological grounds. But I will not enter into the geological discussion preferring to try to give an answer to the question: How can the transmutation of animal remains into oil be imagined?

In order to answer this some thousands of salt water fishes and also shells have been distilled under strong pressure. The result was a liquid, containing mostly nitrogenous bases, such as pyridin, which was little or not at all similar to petroleum. I then recalled some experiments of

Wetherill and Gregory, who found that the wax found in Cadavers, the so-called "Adipocere," was nothing else but the fatty residue, which remains after the putrefaction of all the other animal matter, especially of the nitrogenous constituents of the cadaver. It is also well known that even fossil bones frequently contain fat. The question now raised was this: Could not the process in nature have been a similar one; should not first of all the nitrogenated animal substance have been destroyed leaving the fat, which was then transformed into oil. In order to prove chemically this possibility, I submitted animal fat (train-oil) to distillation—first in a sealed glass tube, later on in a large iron vessel—under a pressure of twenty-five atmospheres at a moderate heat (300-400° C.) and to my great delight found that under favorable conditions seventy per [fol. 1125] cent of the train oil was transformed into petroleum. This equals ninety per cent of the theoretical output. Besides the oil some water and some combustible gas was always formed. The same behavior has been shown by other fats like butter, the fat of hogs, artificial fats, also the chemically pure glycerids of the fats like tri-olein, tri-stearin and the free fatty acids. All could be transformed into petroleum by distillation under pressure, when managed in the proper way.

This liquid, which you see here, is the distillate of the fish oil, and I have isolated from it almost all the hydrocarbons which have been discovered in the petroleum of Pennsylvania. The other products—the oil burning in this small lamp, too—are oils obtained from the crude material by purification.

But not only illuminating oils are produced. I separated also by distillation those lighter hydrocarbons which compose the gasoline, the ligroin, the benzine, etc. Recently I have succeeded in finding and separating paraffin wax and lubricating oils from those parts of the crude oil which show a high boiling point. This removes the objection of O. Ross to my theory of the formation of petroleum from animal remains. As a matter of fact I have found in the distillate obtained by decomposition of train oil, nearly all the constituents which have been separated from the natural crude petroleum, and even the gases, which, like natural gas, consist essentially of marsh gas.

Very recently I have made close investigations on the mechanism or on the chemism of the formation of the hydrocarbons of the petroleum produced by distillation of fat under pressure. This paper is published in a recent number of the Berichte der deutschen chemischen Gesellschaft, 1893, *26*, 1436. These experiments prove that the simpler organic acids split up in the same way, yielding almost the theoretical quantity of the respective hydrocarbons. Thus phenylacetic acid yields toluene. For further details I am obliged to refer to the paper itself. I need only remark, that we have to assume that the acids with high molecular weights are decomposed with the production of a number of hydrocarbons.

To recapitulate, it is a geological fact that we find in nature the remains of antidiluvian animals as shells, fishes, saurians accumulated in masses. Whether these animals have been piled up in consequence of a natural super-production in special places in the ocean, or by currents, or [fol. 1126] in consequence of great revolutions of the earth, this must be decided by geology; but the remains exist.

Now in which manner do the organic substances of these animals become decomposed?

The animal substance consists essentially of nitrogenated material and fat. The former is easily decomposed, the latter is very stable, a fact which has been very well known for a long time and has been shown again by exact investigations. Therefore we find the wax of cadavers in old graves, therefore the fat in the bones of mammals thousands of years old, therefore the fat on the bottom of the ocean recently found.

Whether and how far the fat was decomposed in this long period by the water splitting up gycerol and forming the free acid, for instance the fat in the bones of mammals, cannot be answered. Both, fat as well as the fatty acids form petroleum when distilled under pressure.

We can imagine, that such remains wrapped in mud and transported by the currents in the ocean, easily accumulate and later on, under the pressure of sedimentary layers or strata, perhaps under the influence of heat too, are transformed into petroleum. This is only one of the many possibilities by which the mechanical process of the transmutation of fat into petroleum may have happened.

Under any circumstances I think I have proven that from the chemical standpoint, the formation of petroleum from animal remains has the greatest probability, as we are able now to transform every animal fat into petroleum.

[fol. 1127] TRANSLATION OF PETITIONER'S EXHIBIT No. 154

Derivation of Benzol from Crude Oil and Crude Oil Residues. Chemiker Beitung, 1896, p. 8.

Crude oil, or the products derived therefrom, are subjected to double decomposition, i. e., under varying conditions. The first decomposition is accomplished in a cast iron retort half oval in shape, at comparatively low temperature (about 525-550°) and under ordinary pressure. The retorts are provided with sliding basins (troughs) through which the removal of the coke-like residues is facilitated. The crude oil feeder and the heating of the retorts is regulated by keeping a constant temperature of about 200°, in the vessel connected with the retort, thus, products with a boiling temperature of 200°, are being accumulated in the vessel. These can be used either as fuel, or for other purposes, or, subjected to another decomposition. The hydrocarbons of specific weight 0,8000,810, not retained at a boiling point of 200° in the vessel, pass into the coolingworm, where the solidified products are separately accumulated under the name of "useful tar," while the non condensable gases pass into the gasometer, to be used for heating or motor fuel. The "useful tar," is generally subjected to distillation in a standing retort provided with a small dephlegmator, and the distillates divided into fractions of boiling points 100°,—130°,—160°,—180°,— 200°. The distillate residue passes to the tar drained by the first decomposition into the retort vessel, and is worked up with it. All of the above enumerated fractions enter separately into a second decomposing oven and pass through two retorts of similar construction, as those used by Julius Pintsch, to obtain oil gas. The decomposing temperature is kept for the most easily boiling fractions at 700°, and rises to 1200° for the slowest boiling distillates. The pressure amounts to about 2 Atm., which

is obtained by a flange with a small hole, attached between the second retort and the vessel. This hole necessarily can be cleaned with a spindle governable from the outside. The temperature in the vessel is kept at 150-200°, in order to accumulate the heaviest parts of the aromatic tar [fol. 1128] therein. The products not held back by the vessel pass through a cooler and the solidified parts therein constitute the aromatic tar, containing 30-35% benzol. In order to obtain fractions with narrower boiling points, the contents of the vessel, together with the condensating products flowing off from the cooler, are re-distilled in a retort. The part overflowing at 120° constitutes the so-called raw benzol and can be utilized for the obtainment of anilin oil. The other distillates with boiling temperature of 160-180-200° revert to the second decomposing oven, whereas the fractions of over 200° boiling point can be utilized for the obtainment of naphtha, anthracene, etc. Finally the liquid tar of over 200° boiling point which accumulated in the vessel during the first decomposition of the crude oil, can be divided into fractions in a distilling retort, and transformed into aromatic tar by decomposition and pressure, but the decomposing temperature must be kept considerably higher than for hydrocarbons boiling at 200°; the soot development in the retorts is also larger, and the derived aromatic tar distinguishes itself by a considerably lower benzol content. The total benzol yield, of which the process is capable, should amount to 12% of the total weight of the crude oil used.

[fol. 1129] TRANSLATION OF PETITIONER'S EXHIBIT No. 155

(No. 30. 1902)

About Benzol Fabrication in Russia

By N. Pantjuchow, Chemiker Zeitung Repertorium

1902, p. 317

The extraction of benzol from naphta is a problem that has been accomplished in laboratories for a considerable

time. In order to exploit these results wholesale, the Russian Benzol and Anilin Production Company was established, which built the first factory at Kineschma. Concerning the process itself the following information is at hand. The chromogens, according the process of Nikiforow, are mainly obtained through double distillation of naphtha or naphtha residues, whereby a decomposition of the hydrocarbons is brought about through employment of high temperature and pressure. Two ovens are in use for the first distillation and decomposition, which are constructed for an uninterrupted operation lasting 2-3 days. From the [fol. 1130] first distillation alone approximately 38% of useful tar is obtained, half of which contains aromatic hydrocarbons, and a second distillation already yields benzol, etc. The coke, gases and heavy hydrocarbons obtained from the second distillation are being used for fuel. Generally a yield of 12% in benzol and toluol, 1% anthracene and 2-3% naphthalene is expected from the raw material. The raw benzol yield is twice re-distilled with a view to cleansing the second time in a Savalle column. This benzol is not to be placed upon the market as such, but following a transformation, as anilin. At present the factory is only equipped to work up 100,000,150,000 pood (Russian, slightly over 36 pounds) naphtha or residues, corresponding to 12000-16000 pood benzol. According to an approximate calculation of the management, the production of 1 pood of 90% benzol will cost 1 rubel, and anilin 6 rubels per pood.—It is also pointed out that the Russian benzol is entering the market at an unfavorable time as its prices have dropped, as well as that of its by-products. However, naphtha-benzol might be able to meet competition in the Russian market, as an import duty of 20 kopeks (one kopek, about ½ cent) upon a pood of raw benzol and 1½ rubel (gold) upon a pood of cleansed benzol prevails. In the years 1900-1901 2-3000 pood of benzol were imported. The coloring matter (dyes) produced from the same, are generally imported as half-finished and finished products (anilin and anilin salts). It is here where greater competition will take place. (Industry Zeitung, Riga, Vol. 28, No. 217, 1902).

[fol. 1131] PETITIONER'S EXHIBIT No. 156

FP 848,290 M. Descouhes Pl. Unique

FIG. 1.

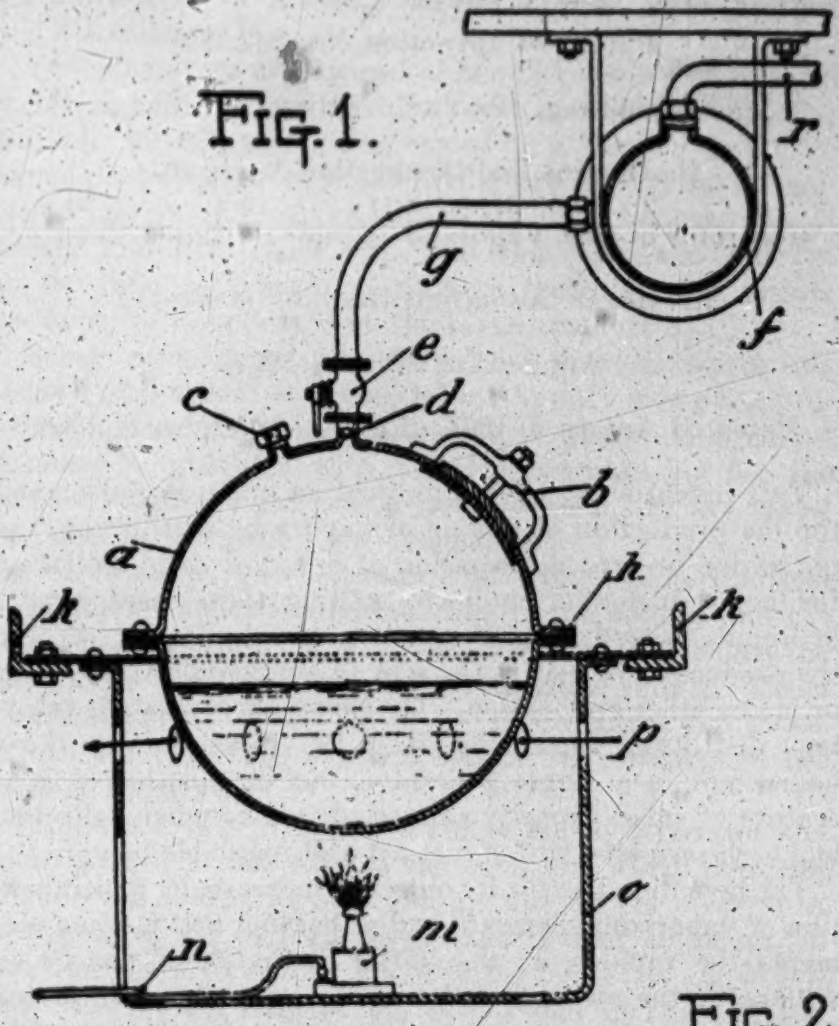
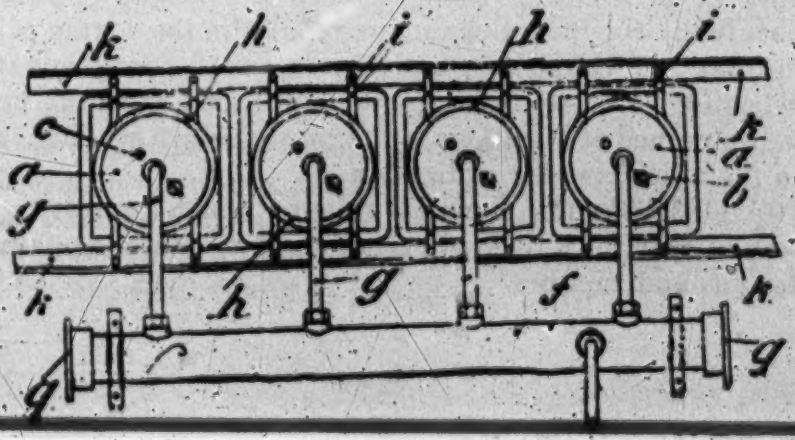


FIG 2



[fol. 1132] TRANSLATION OF PETITIONER'S EXHIBIT No. 156

French Republic, National Office of Industrial Property

Patent of Invention No. 343,390

XV—Lighting, Heating, Cooling, Ventilation

2—Heating and Combustion Apparatus

Generator of Gas, Vapors or Liquids in Closed Vessels

Mr. Roger Desouches, Residing in France

Applied for May 24, 1904

Patented August 4, 1904. Published October 3, 1904

This invention has for its object an apparatus designed for the production of gas or of vapors by distillation, vaporization or even dissociation of liquid or solid bodies or for the production of liquids by melting, these gases, vapors or liquids to be utilized, for example, as hydrocarbons, for the production of motive force in an automobile, in lighting, or in any other application. The invention consists in treating, distilling, vaporizing, heating, dissociating) these bodies not in a single generator, but in a series of generators of small capacity connected to a common collector, and each provided with a distinct and regulable heater.

The invention has for its object to increase, by multiplication of vaporizing elements and of heating and melting elements the rapidity in the initial discharge of gas or of vapors, or the melting of the bodies, as well as the means for regulating the operation of the apparatus; it moreover, enables the isolating of any number of elements to proceed eventually for their cleaning or repairs in the course of operation. It comprises, equally, means for preliminarily reheating the body to be treated and to maintain the products obtained at a suitable temperature before sending them to the apparatus for utilization.

[fol. 1133] In the annexed drawing which represents by way of example a form of execution of generator apparatus for gas and vapors:

Fig. 1 shows one of the generator elements with the collector of gas or of vapors.

Figure 2 shows in plan a battery of generators grouped about a collector.

The generators are formed of closed vessels *a* of suitable material, provided, for charging, with an autoclave opening *b* and an air escape opening closed by a stopper *c*. At the upper part of a gas out take tubulature *d* carrying a regulating valve *e*. These vessels are arranged for example, in a right line before a collector *f* to which they are collected by the tube *g*. They rest through their junction collars on the curbs *i* supported on the brest-summers *k*.

Below each generator there is a heating apparatus formed of a burner *m* connected by the tube *n* to an appropriate source of fuel; this burner is placed in a closed chamber *o*, provided with suitable openings *pp* for the circulation of air and which is suspended, like the vessel elements between the brest-summers *k*.

The vapor or gas collector *k* of elongated, cylindrical form, has a capacity corresponding to the volume and the number of generators *a*. In order to permit of cleaning, the collector is closed at its ends by removable ends *q*. From a suitable point of the periphery, there leaves the vapor or gas out take tube *r* which brings the products to the utilizing apparatus.

In figure 2, is represented a single line of generator elements placed at one side of the collector, which does not exclude the arranging of a similar line on the other side. In the same way, a form other than that of an elongated cylinder as shown can be given to the collector. It is evident that on the path of the tube *r* and in front of the utilizing apparatus can be placed according to circumstances a washer or purifier, carburetor or other analogous apparatus.

The invention is applicable in any case where a rapid and easily regulable production of gas, vapors or liquids is desired for stationary or automobile motors, for lighting, by distillation, disinfection, perfuming, and in general in every industry where gas, vapors or liquids are produced. It is suited to all kinds of generating bodies of gas, of vapors, or of liquids, solid, liquid or powdered.

[fol. 1134] The burner *m* can be any kind, petrol, alcohol, gas, or other. In certain cases, as in automobiles, or vehicles, it might be of interest to be able to easily regulate the heating, in a manner to obtain, either an energetic heating to provide an immediate disengagement of gas or vapors, or a moderate heating to bring about a regular and uniform disengagement; this case occurs also when the gas or vapor generating body is solid, and it is necessary to preliminary bring it to the liquid state to provoke the disengagement of gas or vapors or even when the generating body of motive force is used in the liquid state directly in the mixing chamber of an explosion motor for example. In these circumstances, the regulation of the heating can be realized by the aid of a series of concentric superposed crowns placed below each generating element in immediate contact with the wall of this apparatus. These crowns are carried to a suitable temperature by the aid of an electric current produced by accumulatos, for example, if it is a matter of feeding an automobile engine; in causing the current to circulate in a desired number of these crowns, the quantity of heat destined for heating can be graduated. This arrangement of heaters adhering to the wall itself of the generator is especially advantageous when the generating body of motive force should be preliminarily brought to a state of fusion.

The use of these concentric crowns permits, at need, of the suppression of the exterior source of heat by immersing them in the mass to be treated. When the liquid is sent directly into the mixing chamber, the combination of separate generators should be placed at a suitable level relative to the motor, with the interposition of all necessary organs to maintain and stabilize the outflow of liquid.

The generators can be spherical, elliptical, oblong, or of any other form, coming in a single piece or in several. When the number of these generators is relatively large, the collector is necessarily of relatively able dimensions. In this case, it may be necessary to avoid the cooling of the gas, vapor or liquids before their use; there is then placed around or on all of these collectors appropriate reheaters, combined, for example, with the escaping gas, or even with preliminary heating of the bodies to be treated before their introduction into the generators, the collectors being thus primarily heaters.

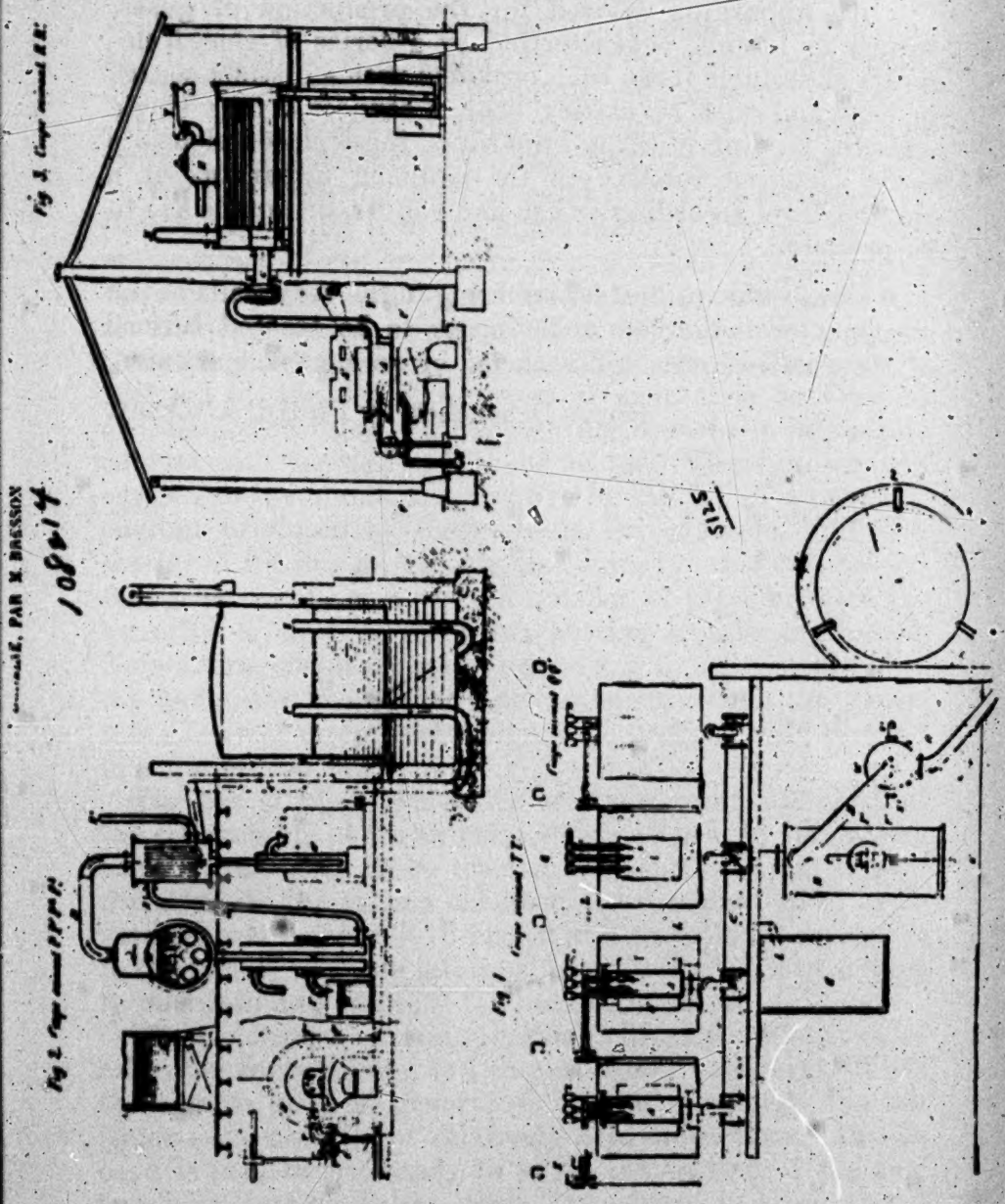
[fol. 1135] Résumé

1. An apparatus devised for the production of gases, vapors or liquids, characterized by a series of closed elements of suitable form, each provided with a distinct source of heat and with regulating organs connected to a single collector feeding utilizing apparatus, these closed elements being disposed relative to the utilizing apparatus at a suitable level according as gas and vapors, or liquids are to be produced.

2. The system of heaters adhering to the very walls of the elements or immersed in the mass to be treated formed of concentric crowns and each fed by an electric current.

Roger Desouches, by Picard, Attorney.

[fol. 1136] PETITIONER'S EXHIBIT No. 157



[fol. 1137] TRANSLATION OF PETITIONER'S EXHIBIT No. 157

Patent No. 108,214. Dated May 29, 1875

A. M. Bresson. For a Process of Manufacturing Benzine

Plate III

For a long time theorical chemistry has known that in projecting hydrocarbons of heavy tar oil on a surface at a red heat, or in causing their vapor to pass through a porcelain tube at a red heat, there is a splitting of the elements composing these heavy oils, which are transformed into illuminating gas and lighter liquid hydrocarbons, principally into benzine; but up to now no practical process or apparatus has been capable of industrial application.

In effect a great practical difficulty presents itself; all liquid thrown onto a surface heated to a red heat immediately causes the temperature to drop, and then this liquid, as heavy oil for example, no longer meets but a surface of which the temperature is lowered, does not decompose, but volatilizes for the most part, and one received on the condensation only heavy oils similar to those used and only traces of benzine.

The object of this invention is a process of manufacture designed to obviate these drawbacks.

I take the jet of oil intermittently and throw it on the lower surface of a retort of cast iron heated to a red heat.

This retort A is of a form analogous to those employed in gas manufacture, but the bottom is formed of two horizontal parts connected by a curve raised as a shelving ridge whose effect operates as two separate apparatus.

The retort, which is raised to a red heat in the furnace A′, is penetrated by two tubes B, B′, ending in a sprinkling head, tubes which communicate with an upper reservoir K filled with heavy oil.

At the start, the tube B is opened; the liquid thrown on the half of the red retort decomposes immediately; but at the end of a quarter of a minute, one closes B to open B′; then a new jet of heavy oil falls on the second part of the bottom of the retort and decomposes in its turn; during this time, the first part, not being hit by a cold liquid, retakes its first temperature; but as after another quarter of [fol. 1138] a minute one closes B′ to open B, and so forth

alternately, one obtains through this means a regular production of hot vapors composed in large part of gas and of light oil containing a large proportion of benzine, because the various parts of the surface of the retort carried to a red heat are hit by the liquid only alternatively and can thus retake the temperature suitable for decomposition.

To obtain the alternate jets, I have made a double valve C, where the arrival of the oil takes place by a single tube L and the departure by the two tubes B, B′.

The cylindrical box E has two holes pierced at right angles; the- communicate respectively with the tubes B, B′ in such a manner that mounting a gear wheel E′ on the box E, meshing with the pinion C′ which carries on its shaft a pulley placed in movement by a belt moved by the horizontal shaft of any suitable motor, I cause the box E to make about one revolution a minute, which having its openings at right angles, opens and closes alternately the tubes B, B′ twice, from which intermissions result from quarter to quarter minute, more or less according to considerations of the apparatus.

Another problem remains to be solved: given a mass of hot vapors escaping from the retorts, it is necessary to liquify them and separate all those that are not light oils.

I obtain this separation exactly by causing these vapors to pass through a kind of tubular boiler H with return tubes.

This boiler is full of water, which the latent heat of the vapors will raise to a high temperature; but as, with the aid of a large safety valve Y, one always maintains the pressure at five atmospheres, all parts of the boiler are at exactly a temperature of 152° Centigrade, so that the hydrocarbons that are liquid at this temperature or higher, only will be liquified and flow out through the siphon tube I; all of the other liquid hydrocarbons whose boiling point is below 152°, remain gaseous and mixed with the incondensible gas.

I then cause the vapors of light oils to pass into a tubular condenser constantly fed with very cold water by a pump for this, where they form to be gathered by a siphon.

The heavy oil to be decomposed is stored in the upper reservoir K from which it flows through the tubes L to be thrown in an intermittent manner into the retorts A by the aid of the special valve C and tubes B, B′ and heated to a red heat in the furnace A′.

The decomposed heavy oil escapes in the state of vapor at a high temperature and is conducted through the tubes D

[fol. 1139] into boxes F, where they pass through a bed of very heavy oil; from there, these vapors are conducted through the tube G into the tubular boiler H maintained at five atmospheres.

In this boiler, all of the tars and heavy oils are condensed and they flow out through the siphon tube I, cooled by a current of cold water in the reservoir J from whence they pass into the reservoir K to be mixed with other heavy oils which are to be again decomposed; or better yet, they will be distilled in apparatus for this purpose and will yield a notable quantity of anthracene, and there are heavy oils obtained in this special distillation which will be sent by a pump into the reservoir K.

The vapors of light oils mixed with combustible gas leaving the tubular boiler through the tube M are directed into a powerful tubular condenser, which is fed with very cold water by a steam pump; this water flows out through an overflow N_2 and serves to cool the tars, as we have already described.

Under the influence of this condensation, all of the light oils, composed in large part of benzine, liquify, and flow out through the siphon tube O into the receiving reservoir O′ of which the contents are consequently formed of crude benzine of good quality, which will then be rectified by the processes ordinarily in use.

The gases composed of non condensible hydrocarbons are conducted through the tubes U into a gasometer V, from which they will be distributed to the furnaces by the tube X.

On these tubes are built, for each of the furnaces A′, three strong out takes Z, which will introduce the gas into burners placed under the retorts where they replace the coal which one will cease to throw onto the grate when the jet of gas furnished by the decomposition of the heavy oils is sufficiently powerful.

Summing up this invention comprises:

1. The double intermittent jet obtained with my valve or all other means in a red hot retort.

2. The application of a tubular boiler under constant pressure which gives a fixed and regular temperature.

3. The use of tubular condensers for the liquifaction of benzines and light oils, these condensers not having yet served except in alcohol distilleries.

4. The combination of the process and of its apparatus which function automatically and are heated by the waste gases provided by the decomposition of the heavy hydrocarbons used as the starting material of our manufacture.

[fol. 1140] TRANSLATION OF PETITIONER'S EXHIBIT No. 158

Dingler's Polytechnische Journal, 1878, Pages 353-358

Concerning the Effect of High Temperatures on Petroleum, Lignite-tar, and Other Similar Materials

By Alexander Letny

From the Laboratory of the Technological Institute of St. Petersburg

In the distillation of petroleum, temperature and pressure have considerable effect on the quality of the distillate. I succeeded in observing that, the higher the temperature of the furnace heating the distilling retort, the more resinous and harder to purify with acids and alkalies is the distillate. This resinification is still more noticeable when the smoke channels in the furnace are higher than the level of the petroleum in the distilling retort, which causes the decomposition of the vapors owing to their coming in contact with the hot walls of the retort. In Pennsylvania, the distilling boilers are constructed with greatly raised heads, whereby a larger yield of easily vaporizing products is obtained, because the petroleum vapors of high boiling point, are being decomposed into more easily evaporating ones. The reverse is the case in the distillation of lignite tar and ozocerite, since a decomposition of the paraffin is to be avoided, the retort and steam exhaust pipe are adjusted as closely to the level of the material to be distilled as possible. If this is not done, the paraffin decomposes. To the same cause may also be ascribed the fact that, in petroleum distillates of high boiling point, the presence of hydrocar-

bons which react with fuming nitric acid is often noticed. Eichler[1] discovered in high boiling portions of Baku petroleum the presence of aromatic hydrocarbons in the course of distillation, hence it is to be assumed that they developed in consequence of decomposition of the vapors through heating. Even the lubricating oil yield derived from petroleum by very careful distillation with superheated steam, reacts with fuming nitric acid. Crude petroleum, on the [fol. 1141] other hand, does not show this reaction. Schorlemmer[2] found aromatic hydrocarbons in Canadian petroleum. Jong converted the high boiling fractions of petroleum directly into easily volatile products by distilling under increased pressure. I succeeded in obtaining easily volatile bodies from heavy petroleum by passing the latter through a tube heated to not over 300°. Similar decomposing experiments were carried on by H. Vohl (No. 177, Vol. 58, 1865) by passing petroleum through a red-hot pipe filled with lime.

If by such relatively unimportant changes in distilling conditions and increased temperatures a difference in the derived products is noticeable, it appeared to me, that by increased pressure and red heat, decomposition must go still further. In order to observe decomposition under varying conditions, I turned directly to the gas factories, where illuminating gas was obtained from petrocene or petroleum residues. It was evident that, besides gas, a tar-like substance was obtained, which did not yield gas by renewed heating. This tar, was not obtained in every retort and in equal quantity, and what is more, in some instances, no residue was found. A steady, even, yield of tar is obtained by the manufacture of the so-called mixed wood-oil gases, which really ought to be called carbon-petrol gas, since the wood carbonizes directly at the beginning of the heating. This gas is widely used in Russia, and not only single factories, but whole cities, like Kiev and Kazan, are being lighted with it. The process consists in passing the petroleum or residues in streams into the red-hot retort filled with wood. The wood absorbs the petroleum which decomposes in consequence of the high temperature before it can touch the walls of the retort. At the conclusion of the operation carbon remains in the retorts and in the vessels a thick petroleum-like mass condenses, which, after

renewed passing into retorts, does not yield gas again. This method is thought advantageous because even separation of the gas is accomplished and no particular attention in regulating the temperature is necessary, as the petroleum does not come into direct contact with the retorts, hence, it is decomposed to a lesser degree than coke which settles upon the walls of the retorts and constitutes one of the main causes of rapid burning-through of the retorts. The tar settles in the hydraulics and cooling pipes. The tar settling near the retorts, i. e., in the hydraulics, is apparently resinous, resembling heavy petroleum residues, but is heavier [fol. 1142] than water. In those pipes distant from the retort and closed to the cooler, there settles an easily mobile liquid of aromatic odor. If this resinous tar is passed a second time into a retort, a very small yield of gas is obtained, but the tar becomes thicker and its density rises from 1.015 to 1.207, and does not change after passing through the retorts anew.

The tar obtained by a second passing of petroleum residues into a wood filled retort of 2 meters length, and 0.285 meters diameter, has all the characteristics of coal tar. When ignited, it burns with a smoky flame, and contains an admixture of coal dust, and on dry distillation commences to boil at 80°. The distillate boiling over at 200° is fluid; at higher temperatures a yield of crystal-like substance is obtained, which solidifies in the cooler. Above 250°, still another liquid goes over. With a rise in temperature above 300°, an oil-like liquid distills, from which crystals separate after cooling. From the parts boiling between 200° and 250° a white substance separated, and its odor reminded of naphthaline. It is soluble in carbon disulphide, petroleum benzine, and ether. If it is crystalized from the solution and sublimed, it melts at 79°. By treatment with crude nitric acid, nitration takes place. The nitro-compound crystalized several times from alcohol, developes yellow crystals of mono-nitro-naphthaline $C_{10}H_7(NO_2)$, which melts at 61°.

The fraction boiling between 80 to 200° was mixed with the liquid filtrate separated from the naphthaline crystals, and treated with sulphuric acid (equal parts of water and acid). The layer separating from the acid upon standing, showed, after treatment with caustic soda and washing with

water, a boiling point of 80°. Upon a fractional distillation one obtained a fraction of a boiling point of from 80° to 100° resembling benzol, and after mixing with Nordhaused sulphuric acid, and heating 24 hours in a water bath, it yielded a substance entirely soluble in water, which is the case with sulpho-benzoic acid.

This substance of 80 to 100° boiling point yielded upon treatment with fuming nitric acid a nitro compound which was reduced by tin and hydrochloric acid to anilin, which, in turn, by treatment with chloride of lime, yielded clear violet colored crystals of mauveine.

The fractions of higher boiling point than 190° react quite similarly with fuming nitric acid whereby they form nitro compounds and with Nordhausen sulphuric acid they [fol. 1143] yield substances soluble in water. From this it will be seen that up to 200°, the distillate consists exclusively of only such products as develope by the dry distillation of coal tar.

It still remained for me to search for other solid tar products of high boiling point. For this purpose, tar of 300° was subjected to distillation until only a dry substance remained in the retort. After cooling, the distillate deposited yellow colored crystals. By cooling and filtration through glass wool, the crystals were separated from the liquid. In cold alcohol they were hardly soluble, while in boiling alcohol they dissolved more easily. After the crystals had been re-crystalized a few times in alcohol, and finally in petroleum ether, they appeared in leaf shape with a mother of pearl gloss. The melting point was 210° (according to Graebe the melting point of anthracene is 213°). The benzol solution of the crystals with a benzol solution of picric acid forms red needle-shaped crystals of the formula $C_{14}H_{10}2C_6H_2(NO_2)_3O$. The melting point is 138°. If this solution and the benzol solution are brought together with dinitro-anthraquinone (von Fritsche reaction), violet crystals develope, characteristic of anthracene. In contact with acetic acid and chromic acid anthraquinone is obtained, of melting point 272°. From the cole alcohol solution filtered from the anthracene crystals, crystals separated upon concentration, resembling those of anthracene. After they were re-crystallized a few times from alcohol, they melted at 96°. Its solution in absolute alcohol yielded with a solu-

tion of picric acid, red crystals of a picric combination which, purified by crystalization, melted at 143°, similar to picric phenyl.

The substance, which, after a treatment with sulphuric acid and potassium bichromate, crystallized out from a 50% solution of acetic acid, melted at 198° (Phenanthraquinone). The liquid parts, which had separated from the anthracene crystals, consisted of unchanged petroleum and benzols.

The tar just described is, as mentioned, a product of rerun petroleum residues run through a red-hot retort. For a comparison, I took the resinous tar of 1.015 specific gravity, which was obtained by a single passing of petroleum through the retort. Upon prolonged settling, the tar separated into two layers, the lower of the consistency of glue, which barely flowed from the vessel and contained much coal dust, and an upper, which flowed easily and resembled petroleum residues. The upper layer began to boil at 125° and through distillation was separated into [fol. 1144] bodies of 125 to 200° and from 200 to 280° boiling points; the latter, like the above described resin, deposited a white crystal-like mass of naphthalenes while cooling off. The part of 250 to 300° boiling point, gave, while cooling, only a small quantity of crystals. The part boiling at 300 to 340° also deposited crystals. Finally, the distillate boiling at 350° was divided into six parts, all of which gave varying quantities of crystals while cooling off. The retort did not endure a further distillation; after cooling, a kind of pitch remained in it, which had a fatty appearance. It was treated with carbon disulphide, and the solution yielded, after distillation, a reddish-yellow heavy mass (petrocene).

The lower dense tar sediment was also treated with carbon bisulphide and yielded, after removing the latter through distillation, the same tar-like mass as the upper one; hence it was subjected, together with the upper layer, to distillation. In the residue, after extraction with carbon disulphide, a sediment of carbon remained.

The fractions boiling up to 250°, after removal of the naphthaline crystals, were treated with caustic soda and sulphuric acid. The resin, which developed through the effect of sodium oxide deposited, after separation from the

distillate, upon admixture of the acid, traces of phenol. The distillate yield of the resin was washed with water and subjected to fractional distillation. The part coming over between 130-145° represented an aromatic, xylol-like liquid of easy nitrating nature. Upon conclusion of the reaction, the mass was dissolved in warm alcohol and evaporated. Needle-like crystals separated, which, recrystallized from alcohol and ether, melted at 123° (di-nitro-xylol). The other parts of the tar, of higher boiling point, were also easy to nitrate. Of the parts coming over up to 200°, considerably less was found than in the first tar; the largest part consisted of liquids of higher boiling point than 250°, and of naphthalene. The liquid going over at 296-350° yielded while cooling off, a green-white mass of crystals, as also those of boiling points over 350°. After all solid parts were separated from the liquid ones, and the former re-crystallized from alcohol and ether, there was obtained a mass in the shape of bright small fish-scales, of green fluorascene. The melting point was 198° (anthrancene). A solution of this mass in benzol with a solution of picric acid formed red crystals of $C_{14}H_{2}2C_{6}H_{3}(NO_{2})_{3}O$ to develope. The same solution yielded with [fol. 1145] Fritsche's reaction, violet crystals, which are characteristic of anthracene.

The alcohol solution, which settled upon the solution of the anthracene, yielded crystals of phenanthrene; this alcohol solution was treated similarly to the alcohol solution of the first resin.

Hence both tars contain the same products as are obtained by the dry distillation of coal tar; naturally with the exception of ammonia. The first tar, after being heated for a considerable time, had a higher specific weight. The second tar, not heated to such an extent, contained a considerably larger quantity of unchanged petroleum, and less solid anthracene and phenanthrene. The heavier weight of the high boiling fractions over those of lower boiling point is caused by tar passing into cooler in a hot condition, and those of lower boiling point can not condense as quickly and are carried off as vapors by the gas. In the pipes of the cooler, a light aromatic liquid, actually condenses, which has a specific weight of 0.904.

It begins to boil at 73°, and the largest part goes over up to 226°, and, finally, very little carbon remains in the retort.

The distillate distilling up to 226° was separated by crystallization, from the other distillate, and washed with sulphuric acid (50% water). The resinous residue derived was separated from the transparent liquid by use of a separating funnel. By an application of caustic soda upon the sediment a yield of oil-like drops of an alkaline liquid of aromatic odor was obtained. If the resin is distilled over slaked lime, only a very small quantity of alkali distillate is obtained, which makes it impossible to ascertain its composition.

(Here follows Exhibits Nos. 159 and 160, side folios 1146, 1147, 1148, 1149, 1150, 1151, and 1152)

[fol. 1146]

EXHIBIT No. 159

Oct. 26, 1925

Walter N. Carpenter, Shorthand Reporter, as Corrected

Indiana Co. patents:

Interrogatory	Patentee	Patent No.	Claims	Texas Company				Standard of Indiana						Bu pr
				HM No. 1	HM No. 2	Hall	Approval	S. R.	S. B. T.	T. R.	T. B. T.	H. P.	Cont.	
1	Lang	954575	1-7	No	No	No	No	No	No	No	No	No	No	
2	Burton	1049667	1-2	Q	Q	No	Q	U	U	U	U	Q	Q	
3	Burton	1055707	1-2	No	No	No	No	U	U	U	U	U	U	
4	Burton	1105961	1-2	Q	Q	No	Q	U	U	U	U	Q	Q	Sc
5	Burton	1112113	1-2	No	No	No	No	No	No	No	No	No	No	
6	Clark	1119496	1	No	UL	No	Yes	No	No	U	U	U	No	
			2-3	No	Q	No	Q	No	No	U	U	No	No	
7	Humphreys	1119700	1-2	U	U	No	Yes	U	U	U	U	U	U	
8	Humphreys	1122002	1-5	No	No	No	No	U	U	No	No	No	No	F, Sc
9	Humphreys	1122003	1-4	No	No	No	No	U	U	No	No	No	No	F, Sc
10	Rogers & Cooke	1122220	1-19	No	No	No	No	Ua	No	Ua	No	No	No	
11	Clarke	1129034	1-6	No	No	No	No	U	U	U	U	U	No	
12	Moore	1130318	1	No	No	No	No	U	No	U	No	No	No	F, Sc
13	Clarke	1132163	1-4	No	No	No	No	U	U	U	U	U	No	
14	Burton	1160689	1-3	UL	U	No	Yes	U	U	U	U	Q	U	
15	Cash	1230065	1-3	UL	No	No	No	Ua	No	No	No	No	No	
16	Humphreys & Burton	1343674	1-3	No	No	No	No	No	No	No	No	No	No	
17	Lewis & Cooke	1392584	1-5 & 7	No	U	No	Yes	No	U	No	U	No	U	F
			6	No	U	No	Yes	No	U	No	U	No	U	F
18	Burton & Clarke	1448254	1-2	No	UL	No	No	Us	Us	Us	Us	Qs	No	Sc
			3-4	No	UL	No	No	No	No	No	No	No	Q	
			5-6	No	U	No	Yes	No	No	No	No	U	U	
19	Clarke	1388514	1-4	No	No	No	No	Us	Us	U	U	U	No	
20	Palmer	1187380	1-3	No	No	No	No	Q	Q	Q	Q	Q	No	
21	Palmer	1313009	1-3	No	No	No	No	No	No	No	No	No	No	
22	Palmer	1360973	1-4	No	No	No	No	No	No	No	No	No	No	
	New Jersey Co. patents:													
23	Wells	1187874	1-6	No	No	No	No	No	No	No	No	No	No	
24	Wells	1232454	1-10	No	No	No	No	No	No	No	No	No	No	
25	Wells	1248225	1-3	No	No	No	No	No	No	No	No	No	No	
26	Ellis	1216971	1-6	No	No	No	No	No	No	No	No	No	No	
27	Ellis	1249278	1-9	No	No	No	No	No	No	No	No	No	No	
28	Ellis	1317868	1-23	No	No	No	No	No	No	No	No	No	No	
29	Ellis	1341975	1-11	No	No	No	No	No	No	No	No	No	No	
[fol. 1147]														
30	Ellis	1396999	1-12	No	No	No	No	No	No	No	No	No	No	
31	Ellis	1415232	1	U	U	No	Yes	No	No	No	No	No	U	
			2, 5, 9, 10	No	No	No	No	No	No	No	No	No	No	
			3	No	No	No	No	No	No	No	No	No	No	
			4, 6, 8	Q	Q	No	Q	No	No	No	No	No	U	

EXHIBIT No. 159

Oct. 26, 1925

Walter N. Carpenter, Shorthand Reporter, as Corrected

atents:

	Patent No.	Claims	Texas Company				Standard of Indiana						Standard of N. J.		
			HM No. 1	HM No. 2	Hall	Approval	S. B.	S. B. T.	T. R.	T. B. T.	H. P.	Cont.	Burton process	Tube and tank process	Gasoline Products Co.
.....	954575	1-7	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1049667	1-2	Q	Q	No	Q	U	U	U	U	Q	Q	Yes	No	No
.....	1055707	1-2	No	No	No	No	U	U	U	U	U	U	No	No	No
.....	1105961	1-2	Q	Q	No	Q	U	U	U	U	Q	Q	Some ext.	No	No
.....	1112113	1-2	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1119496	1	No	UL	No	Yes	No	No	U	U	U	No	Yes	No	No
		2-3	No	Q	No	Q	No	No	U	U	No	No	Yes	No	No
.....	1119700	1-2	U	U	No	Yes	U	U	U	U	U	U	Yes	No	No
.....	1122002	1-5	No	No	No	No	U	U	No	No	No	No	F, Some ext.	No	No
.....	1122003	1-4	No	No	No	No	U	U	No	No	No	No	F, Some ext.	No	No
.....	1122220	1-19	No	No	No	No	Ua	No	Ua	No	No	No	No	No	No
.....	1129034	1-6	No	No	No	No	U	U	U	U	U	No	Yes	Q	No
.....	1130318	1	No	No	No	No	U	No	U	No	No	No	F, Some ext.	No	No
.....	1132163	1-4	No	No	No	No	U	U	U	U	U	No	Yes	No	No
.....	1160689	1-3	UL	U	No	Yes	U	U	U	U	Q	U	Yes	No	No
.....	1230065	1-3	UL	No	No	No	Ua	No	No	No	No	No	No	No	No
on.....	1343674	1-3	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1392584	1-5 & 7	No	U	No	Yes	No	U	No	U	No	U	Formerly	Q	No
		6	No	U	No	Yes	No	U	No	U	No	U	Formerly	No	No
.....	1448254	1-2	No	UL	No	No	Us	Us	Us	Us	Qs	No	Some ext.	No	No
		3-4	No	UL	No	No	No	No	No	No	No	Q	No	No	No
		5-6	No	U	No	Yes	No	No	No	No	U	U	No	Q	No
.....	1388514	1-4	No	No	No	No	Us	Us	U	U	U	No	Yes	No	No
.....	1187380	1-3	No	No	No	No	Q	Q	Q	Q	Q	No	Q	Q	No
.....	1313009	1-3	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1360973	1-4	No	No	No	No	No	No	No	No	No	No	No	No	No
o. patents:															
.....	1187874	1-6	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1232454	1-10	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1248225	1-3	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1216971	1-6	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1249278	1-9	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1317868	1-23	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1341975	1-11	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1396999	1-12	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1415232	1	U	U	No	Yes	No	No	No	No	No	U	No	Yes	Yes
		2, 5, 9, 10	No	No	No	No	No	No	No	No	No	No	No	Yes	Yes
		3	No	No	No	No	No	No	No	No	No	No	No	F, not now	No
		4, 6, 8	Q	Q	No	Q	No	No	No	No	No	U	No	Yes	Yes

[fol. 1147]

30	Ellis	1396999	1-12	No	No	No	No	No	No	No	No	No	No
31	Ellis	1415232	1	U	U	No	Yes	No	No	No	No	No	U
			2, 5, 9, 10	No	No	No	No	No	No	No	No	No	No
			3	No	No	No	No	No	No	No	No	No	No
			4, 6, 8	Q	Q	No	Q	No	No	No	No	No	U
			7	No	No	No	No	No	No	No	No	No	No
32	Clarke	1405286	1-8	No	No	No	No	No	No	No	No	No	No F,
33	Clarke	1410797	1	No	QL	No	No	No	No	No	No	No	Q
			2-4	No	No	No	No	No	No	No	No	No	No
34	Clarke	1413899	1-6	No	No	No	No	No	No	No	No	No	No
35	Clarke et al	1478102	1-7	No	No	No	No	No	No	No	No	No	No
	Texas Company patents:												
36	Adams	1320354	(1-8) (10-12)										
			21, 22 (25-28)	No	No	No	No	No	No	No	No	No	No
			9	Q	Q	No	Q	Qa	No	Q	Q	Q	Q
			13, 14	U	U	No	Yes	No	No	U	U	U	U
			15	U	U	No	Yes	Qa	Qa	Q	Q	Q	Q
			16	U	U	No	Yes	No	No	Q	Q	Q	Q
			17, 23	Q	Q	No	Q	Q	Q	Q	Q	Q	Q
			18, 19	U	U	No	Yes	No	No	No	No	U	U
			20	U	U	No	Yes	No	No	No	No	No	U
			24	Q	Q	No	Q	No	No	Q	Q	Q	Q
37	Adams	1320726	1-5, 8-11	No	No	No	No	No	No	No	No	No	No
			6	No	No	No	No	No	No	No	No	No	U
			7	No	No	No	No	No	No	No	No	No	Q
38	Adams	1320727	1, 3, 5 (8-24), 26, 27, 28	No	No	No	No	No	No	No	No	No	No
			2, 4	No	No	No	No	No	No	Q	Q	Q	Q
			6, 7	No	No	No	No	No	No	No	No	No	Q
			25	No	No	No	No	No	No	No	No	No	Q
39	Adams	1327263	1	U	U	No	Yes	Qa	Qa	Q	Q	Q	Q
			3, 13, 14	No	UL	No	Yes	No	No	No	No	No	No
			4, 5	U	U	No	Yes	Qa	Qa	Q	Q	Q	Q
			6, 7	U	U	No	Yes	No	No	Q	Q	Q	Q
			8	U	U	No	Yes	No	No	U	U	U	U
			9, 10, 12, 15, 24	U	U	No	Yes	No	No	Q	Q	Q	Q
			11, 19, 20, 21, 22, 23	U	U	No	Yes	No	No	No	No	No	Q
			16	U	U	No	Yes	No	No	No	No	No	Q
			17, 18	No	No	No	No	No	No	Q	Q	Q	Q
			24	U	U	No	Yes	No	No	Q	Q	Q	Q
			25	U	U	No	Yes	Qa	Qa	Q	Q	Q	Q
			26-29	U	U	No	Yes	Q	Q	Q	Q	Q	Q
			30	U	U	No	Yes	No	No	No	No	No	No
			31	U	U	No	Yes	No	No	No	No	No	U

	1396999	1-12	No	No	No	No	No	No	No	No	No	No	No	No	No
	1415232	1	U	U	No	Yes	No	No	No	No	No	U	No	Yes	Yes
		2, 5, 9, 10	No	No	No	No	No	No	No	No	No	No	No	Yes	Yes
		3	No	No	No	No	No	No	No	No	No	No	No	F, not now	No
		4, 6, 8	Q	Q	No	Q	No	No	No	No	No	U	No	Yes	Yes
		7	No	No	No	No	No	No	No	No	No	No	No	F, not now	Yes
	1405286	1-8	No	No	No	No	No	No	No	No	No	No	F, not now	No	No
	1410797	1	No	QL	No	No	No	No	No	No	No	Q	No	No	No
		2-4	No	No	No	No	No	No	No	No	No	No	No	No	No
	1413899	1-6	No	No	No	No	No	No	No	No	No	No	No	No	No
	1478102	1-7	No	No	No	No	No	No	No	No	No	No	No	F, not now	No
any patents:															
	1320354	(1-8) (10-12)													
		21, 22 (25-28)	No	No	No	No	No	No	No	No	No	No	No	No	No
		9	Q	Q	No	Q	Qa	No	Q	Q	Q	Q	Q	No	No
		13, 14	U	U	No	Yes	No	No	U	U	U	U	U	Q	No
		15	U	U	No	Yes	Qa	Qa	Q	Q	Q	Q	Q	No	No
		16	U	U	No	Yes	No	No	Q	Q	Q	Q	Q	No	No
		17, 23	Q	Q	No	Q	Q	Q	Q	Q	Q	Q	Q	Q	No
		18, 19	U	U	No	Yes	No	No	No	No	U	U	No	No	No
		20	U	U	No	Yes	No	No	No	No	No	U	No	No	No
		24	Q	Q	No	Q	No	No	Q	Q	Q	Q	Q	Q	No
	1320726	1-5, 8-11	No	No	No	No	No	No	No	No	No	No	No	No	No
		6	No	No	No	No	No	No	No	No	No	U	No	Q	No
		7	No	No	No	No	No	No	No	No	No	Q	No	Q	No
	1320727	1, 3, 5 (8-24), 26, 27, 28	No	No	No	No	No	No	No	No	No	No	No	No	No
		2, 4	No	No	No	No	No	No	Q	Q	Q	Q	Q	Q	No
		6, 7	No	No	No	No	No	No	No	No	No	Q	No	Q	No
		25	No	No	No	No	No	No	No	No	No	Q	No	No	No
	1327263	1	U	U	No	Yes	Qa	Qa	Q	Q	Q	Q	Q	No	No
		3, 13, 14	No	UL	No	Yes	No	No	No	No	No	No	No	No	No
		4, 5	U	U	No	Yes	Qa	Qa	Q	Q	Q	Q	Q	No	No
		6, 7	U	U	No	Yes	No	No	Q	Q	Q	Q	Q	No	No
		8	U	U	No	Yes	No	No	U	U	U	U	U	Q	No
		9, 10, 12, 15, 24	U	U	No	Yes	No	No	Q	Q	Q	Q	Q	No	No
		11, 19, 20, 21, 22, 23	U	U	No	Yes	No	No	No	No	No	Q	No	No	No
		16	U	U	No	Yes	No	No	No	No	No	Q	No	No	No
		17, 18	No	No	No	No	No	No	Q	Q	Q	Q	Q	No	No
		24	U	U	No	Yes	No	No	Q	Q	Q	Q	Q	No	No
		25	U	U	No	Yes	Qa	Qa	Q	Q	Q	Q	Q	No	No
		26-29	U	U	No	Yes	Q	Q	Q	Q	Q	Q	Q	No	No
		30	U	U	No	Yes	No	No	No	No	No	No	No	No	No
		31	U	U	No	Yes	No	No	No	No	No	U	No	No	No

Interrogatory	Patentee	Patent No.	Claims	Texas Company				Standard of Indiana						Bu pr
				HM No. 1	HM No. 2	Hall	Approval	S. R.	S. B. T.	T. R.	T. B. T.	H. P.	Cont.	
	Texas Company patents—Continued:													
40	Adams	1428311	1-9	No	No	No	No	No	No	No	No	No	No	
41	Adams	1428312	1-7	No	No	No	No	No	No	No	No	No	No	
42	Manley	1428338	1-8	No	No	No	No	No	No	No	No	No	No	
			9	No	Q	No	Q	No	No	No	No	No	No	
43	Manley	1428339	1-11	No	No	No	No	No	No	No	No	No	No	
44	Adams	1433519	1, 2	U	U	No	Yes	No	No	No	No	No	U	
			2	U	U	No	Yes	No	No	No	No	No	Q	
			3	U	U	No	Yes	Qa	Qa	Q	Q	U	U	
			4	U	U	No	Yes	No	No	No	No	Q	Q	
			5, 28	U	U	No	Yes	No	No	No	No	No	Q	
			6	U	U	No	Yes	Q	Q	Q	Q	Q	Q	
			7, 11	U	U	No	Yes	Q	Q	Q	Q	Q	U	
			8, 9	U	U	No	Yes	Qa	Qa	Q	Q	Q	U	
			10	U	U	No	Yes	U	U	U	U	U	U	
			12-17, 21-23, 25, 27	U	U	No	Yes	No	No	No	No	No	U	
			18, 19	No	UL	No	Yes	No	No	No	No	No	Q	
			20, 24, 26	No	No	No	No	No	No	No	No	No	No	
45	Adams	1445281	1-9	No	No	No	No	No	No	No	No	No	No	
46	Adams	1455376	1-9	No	No	No	No	No	No	No	No	No	No	
47	Adams	1455377	1-14	No	No	No	No	No	No	No	No	No	No	
48	Adams	1461017	1-3, 13-15, 17	U	U	No	Yes	No	No	No	No	No	U	
			4	No	No	No	No	No	No	No	No	No	Q	
			5, 7-9	U	U	No	Yes	No	No	No	No	No	Q	
			16, 20, 22	Q	Q	No	Q	No	No	No	No	No	Q	
			6	No	No	No	No	No	No	No	No	No	No	
			10, 11, 18	Q	Q	No	Q	No	No	No	No	No	No	
			12	No	UL	No	Yes	No	No	No	No	No	No	
			19	U	U	No	Yes	No	No	No	No	No	No	
			21	U	U	No	Yes	No	No	No	No	No	Q	
49	Manley	1462143	1-6	No	No	No	No	No	No	No	No	No	No	
			7, 8	No	Q	No	Q	No	No	No	No	No	U	
50	Adams	1462677	1-31	No	No	No	No	No	No	No	No	No	No	
			32	No	No	No	No	No	No	No	No	No	Q	
51	Adams	1462678	1-22	No	No	No	No	No	No	No	No	No	No	
			23	No	No	No	No	No	No	No	No	No	Q	
[fol. 1149]														
52	Adams	1477860	1-5	No	No	No	No	No	No	No	No	No	No	
53	Hall	1175909	1-8, 10-12, 14-17	No	No	No	No	No	No	No	No	No	No	
			9, 18	No	No	U	No	No	No	No	No	No	No	
			13	No	No	U	No	No	No	No	No	No	No	

	Patent No.	Claims	Texas Company				Standard of Indiana						Standard of N. J.		
			HM No. 1	HM No. 2	Hall	Approval	S. R.	S. B. T.	T. R.	T. B. T.	H. P.	Cont.	Burton process	Tube and tank process	Gasoline Products Co.
s—Continued:															
....	1428311	1-9	No	No	No	No	No	No	No	No	No	No	No	No	No
....	1428312	1-7	No	No	No	No	No	No	No	No	No	No	No	No	No
....	1428338	1-8	No	No	No	No	No	No	No	No	No	No	No	No	No
		9	No	Q	No	Q	No	No	No	No	No	No	No	No	No
....	1428339	1-11	No	No	No	No	No	No	No	No	No	No	No	No	No
....	1433519	1, 2	U	U	No	Yes	No	No	No	No	No	U	No	No	No
		2	U	U	No	Yes	No	No	No	No	No	Q	No	No	No
		3	U	U	No	Yes	Qa	Qa	Q	Q	U	U	Q	No	No
		4	U	U	No	Yes	No	No	No	No	Q	Q	No	No	No
		5, 28	U	U	No	Yes	No	No	No	No	No	Q	No	No	No
		6	U	U	No	Yes	Q	Q	Q	Q	Q	Q	Q	No	No
		7, 11	U	U	No	Yes	Q	Q	Q	Q	Q	U	Q	No	No
		8, 9	U	U	No	Yes	Qa	Qa	Q	Q	Q	U	Q	No	No
		10	U	U	No	Yes	U	U	U	U	U	U	Yes	Q	No
		12-17, 21-23, 25, 27	U	U	No	Yes	No	No	No	No	No	U	No	No	No
		18, 19	No	UL	No	Yes	No	No	No	No	No	Q	No	No	No
		20, 24, 26	No	No	No	No	No	No	No	No	No	No	No	No	No
....	1445281	1-9	No	No	No	No	No	No	No	No	No	No	No	No	No
....	1455376	1-9	No	No	No	No	No	No	No	No	No	No	No	No	No
....	1455377	1-14	No	No	No	No	No	No	No	No	No	No	No	No	No
....	1461017	1-3, 13-15, 17	U	U	No	Yes	No	No	No	No	No	U	No	No	No
		4	No	No	No	No	No	No	No	No	No	Q	No	No	No
		5, 7-9	U	U	No	Yes	No	No	No	No	No	Q	No	No	No
		16, 20, 22	Q	Q	No	Q	No	No	No	No	No	Q	No	No	No
		6	No	No	No	No	No	No	No	No	No	No	No	No	No
		10, 11, 18	Q	Q	No	Q	No	No	No	No	No	No	No	No	No
		12	No	UL	No	Yes	No	No	No	No	No	No	No	No	No
		19	U	U	No	Yes	No	No	No	No	No	No	No	No	No
		21	U	U	No	Yes	No	No	No	No	No	Q	No	No	No
....	1462143	1-6	No	No	No	No	No	No	No	No	No	No	No	No	No
		7, 8	No	Q	No	Q	No	No	No	No	No	U	No	No	No
....	1462677	1-31	No	No	No	No	No	No	No	No	No	No	No	No	No
		32	No	No	No	No	No	No	No	No	No	Q	No	No	No
....	1462678	1-22	No	No	No	No	No	No	No	No	No	No	No	No	No
		23	No	No	No	No	No	No	No	No	No	Q	No	No	No
....	1477860	1-5	No	No	No	No	No	No	No	No	No	No	No	No	No
....	1175909	1-8, 10-12, 14-17	No	No	No	No	No	No	No	No	No	No	No	No	No
		9, 18	No	No	U	No	No	No	No	No	No	No	No	Q	No

52	Adams	1477860	1-5	No	No	No	No	No	No	No	No	No	No
53	Hall	1175909	1-8, 10-12, 14-17	No	No	No	No	No	No	No	No	No	No
			9, 18	No	No	U	No	No	No	No	No	No	No
			13	No	No	U	No	No	No	No	No	No	No
54	Hall	1175910	9, 11-15, 17	No	No	Q	No	No	No	No	No	No	No
			1-8, 10, 16	No	No	No	No	No	No	No	No	No	No
55	Hall	1194289	1-11	No	No	No	No	No	No	No	No	No	No
56	Hall	1242795	1	No	No	No	No	No	No	No	No	No	No
			2, 4-7	No	No	No	No	No	No	No	No	No	No
			3, 8, 9	No	No	No	No	Q	Q	Q	Q	Q	Q
57	Hall	1242796	1, 3, 5-15, 17, 18, 20, 22, 23, 24	No	No	No	No	No	No	No	No	No	No
			4, 16, 21	No	No	No	No	No	No	No	No	No	No
			2, 19	No	No	U	No	No	No	No	No	No	No
58	Hall	1285136	1-7	No	No	U	No	No	No	No	No	No	No
59	Hall	1261930	1-2	No	No	No	No	No	No	No	No	No	No
60	De Florez	1437045	1, 3, 5, 6	No	No	U	No	No	No	No	No	No	No
			2, 4	No	No	No	No	No	No	No	No	No	No
61	Adams	1506877	1-31	No	No	No	No	No	No	No	No	No	No
62	Adams	1506878	1-13	No	No	No	No	No	No	No	No	No	No
	Gasoline Products Co. patents:												
63	Cross	1203312	1-6	No	No	No	No	No	No	No	No	No	No
64	Cross	1326851	1	No	No	No	No	No	No	No	No	No	No
65	Cross	1423500	1-15	No	No	No	No	No	No	No	No	No	No
66	Cross	1437229	1	No	No	No	No	No	No	No	No	No	No
	Miscellaneous patents:												
67	Chamberlain	1221790	1-25	No	No	No	No	Q	Q	Q	Q	No	No
68	Clarke	1413260	1-9	No	No	No	No	No	No	No	No	No	No
	Products patents:												
70	Ellis	1318060	1-15	U	U	U	Yes	Q	Q	Q	Q	Q	...
	Hall	1239099	16-45	No	No	U(?)	No	No	No	No	No	No	...
	Hall	1239100	46-64	No	No	U(?)	No	No	No	No	No	No	...
	Ellis	1396999	65-66	No	No	No	No	No	No	No	No	No	...
	Clarke	1413260	67-68	No	No	No	No	No	No	No	No	No	...
71–75	Ellis	1318061	...	U	U	...	U	U	U	U	U	U	...
76	Burton	1167884	...	U	U	...	U	U	U	U	U	...	...
77	Burton	1167884	...	Q	Q	...	Q	U	U	U	U	...	...
78	Burton	1167884	...	U	U	...	...	...	F, not now	F, not now	F, not now	F not now	F, not now

.....	1477860	1-5	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1175909	1-8, 10-12, 14-17	No	No	No	No	No	No	No	No	No	No	No	No	No
		9, 18	No	No	U	No	No	No	No	No	No	No	No	Q	No
		13	No	No	U	No	No	No	No	No	No	No	No	No	No
.....	1175910	9, 11-15, 17	No	No	Q	No	No	No	No	No	No	No	No	No	No
		1-8, 10, 16	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1194289	1-11	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1242795	1	No	No	No	No	No	No	No	No	No	No	No	Q	No
		2, 4-7	No	No	No	No	No	No	No	No	No	No	No	No	No
		3, 8, 9	No	No	No	No	Q	Q	Q	Q	Q	Q	Q	Q	No
.....	1242796	1, 3, 5-15, 17, 18, 20, 22, 23, 24	No	No	No	No	No	No	No	No	No	No	No	No	No
		4, 16, 21	No	No	No	No	No	No	No	No	No	No	No	Q	No
		2, 19	No	No	U	No	No	No	No	No	No	No	No	No	No
.....	1285136	1-7	No	No	U	No	No	No	No	No	No	No	No	No	No
.....	1261930	1-2	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1437045	1, 3, 5, 6	No	No	U	No	No	No	No	No	No	No	No	No	No
		2, 4	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1506877	1-3	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1506878	1-13	No	No	No	No	No	No	No	No	No	No	No	No	No
oducts Co. patents:															
.....	1203312	1-6	No	No	No	No	No	No	No	No	No	No	No	No	Yes
.....	1326851	1	No	No	No	No	No	No	No	No	No	No	No	No	No
.....	1423500	1-15	No	No	No	No	No	No	No	No	No	No	No	Q	Yes
.....	1437229	1	No	No	No	No	No	No	No	No	No	No	No	No	Yes
us patents:															
.....	1221790	1-25	No	No	No	No	Q	Q	Q	Q	No	No	...	No	No
.....	1413260	1-9	No	No	No	No	No	No	No	No	No	No	Yes	...	No
tents:															
.....	1318060	1-15	U	U	U	Yes	Q	Q	Q	Q	Q	...	U	U	No
.....	1239099	16-45	No	No	U(?)	No	No	No	No	No	No	...	No	No	No
.....	1239100	46-64	No	No	U(?)	No	No	No	No	No	No	...	No	No	No
.....	1396999	65-66	No	No	No	No	No	No	No	No	No	...	No	No	No
.....	1413260	67-68	No	No	No	No	No	No	No	No	No	...	U	U	No
.....	1318061		U	U	...	U	U	U	U	U	U	...	U	U	No
.....	1167884		U	U	...	U	U	U	U	U	...	...	Yes	...	No
.....	1167884		Q	Q	...	Q	U	U	U	U	...	...	Yes	...	No
.....	1167884		U	U	...	...	...	F, not now	F, not now	F, not now	F not now	F, not now	Yes	...	No

[fol. 1150]

Exhibit No. 160

Oct. 26, 1925

Walter N. Carpenter, Shorthand Reporter, as Corrected

Chart Showing Patents, Other Than Its Own, Used by Each Primary Defendant in the Operation of Its Own Processes and Apparatus

Interrogatory	Patentee	Patent No.	Claims	Texas Company		Standard of Indiana						Standard of N. J., tube and tank process	Gasoline Products Co.
				HM No. 1	HM No. 2	S R	S B T	T R	T B T	H P	Cont.		
	Indiana Co. patents:												
2	Burton	1049667	1-2	Q	Q	U	U	U	U	Q	Q	..	..
4	Burton	1105961	1-2	Q	Q	U	U	U	U	Q	Q	..	..
6	Clark	1119496	1	..	UL	..	..	U	U	U	..	..	..
			2-3	..	Q	..	U	U	U	..	..	..	..
7	Humphreys	1119760	1-2	U	U	U	U	U	U	U	U	..	..
11	Clarke	1129034	1-6	..	..	U	U	U	U	U	..	Q	..
14	Burton	1160689	1-3	UL	U	U	U	U	U	Q	U	..	..
17	Lewis & Cooke	1392584	1-5 & 7	..	U	..	U	..	U	..	U	Q	..
			6	..	U	..	U	..	U	..	U	..	..
18	Burton & Clarke	1448254	1-2	..	UL	Us	Us	Us	Us	Qs	..	..	..
			3-4	..	UL	..	..	..	..	..	Q	..	..
			5-6	..	U	..	..	..	..	..	U	Q	..
20	Palmer	1187380	1-3	..	..	Q	Q	Q	Q	Q	U	Q	..
	New Jersey Co. patents:												
31	Ellis	1415232	1	U	U	..	..	..	..	..	U	Yes	Yes
			2, 5, 9, 10	..	..	..	..	..	..	..	..	Yes	Yes
			4, 6, 8	Q	Q	..	..	..	..	..	U	Yes	Yes
			7	..	..	..	..	..	..	..	..	F, not now	Yes
33	Clarke	1410797	1	..	QL	..	..	..	..	..	Q	..	..
	Texas Company patents:												
36	Adams	1320354	9	Q	Q	Qa	..	Q	Q	Q	Q	..	..
			13-14	U	U	..	..	U	U	U	U	Q	..
			15	U	U	Qa	Qa	Q	Q	Q	Q	..	..
			16	U	U	..	..	Q	Q	Q	Q	..	..
[fol. 1151]													
			17, 23	Q	Q	Q	Q	Q	Q	Q	Q	Q	..
			18, 19	U	U	..	..	..	..	U	U	..	..
			20	U	U	..	..	..	..	..	U	..	..
			24	Q	Q	..	..	Q	Q	Q	Q	Q	..
37	Adams	1320726	6	..	..	..	..	..	..	..	U	Q	..
			7	..	..	..	..	..	..	..	Q	Q	..
38	Adams	1320727	2, 4	..	..	..	..	Q	Q	Q	Q	Q	..
			6, 7	..	..	..	..	..	..	..	Q	Q	..
			25	..	..	..	..	..	..	..	Q	..	..
[illegible]	[illegible]	1397263	1, 2	U	U	Qa	Qa	Q	Q	Q	Q	..	..

37	Adams	1320726	6	..	..	..	..	..	..	..	U	Q	..	..
			7	..	..	..	..	..	..	..	Q	Q	..	..
38	Adams	1320727	2, 4	..	..	..	..	Q	Q	Q	Q	Q	..	..
			6, 7	..	..	..	..	..	..	..	Q	Q	..	..
			25	..	..	..	..	..	..	..	Q	..	..	..
39	Adams	1327263	1, 2	U	U	Qa	Qa	Q	Q	Q	Q	..	..	..
			4, 5	U	U	Qa	Qa	Qa	Qa	Q	Q	No	..	..
			6, 7	U	U	..	..	Q	Q	Q	Q	No	..	..
			8	U	U	..	..	U	U	U	U	Q	..	..
			9, 10, 12, 13, 24	U	U	..	..	Q	Q	Q	Q	..	..	..
			11, 19, 20, 21, 22, 23	U	U	..	..	..	..	..	Q	..	..	..
			16	U	U	..	..	..	..	..	Q	..	..	..
			17, 18	..	..	..	..	Q	Q	Q	Q	..	..	..
			24	U	U	..	..	Q	Q	Q	Q	..	..	..
			25	U	U	Qa	Qa	Q	Q	Q	Q	..	..	..
			26-29	U	U	Q	Q	Q	Q	Q	Q	..	..	..
			31	U	U	..	..	..	..	..	U	..	..	..
44	Adams	1433519	1	U	U	..	..	..	..	..	U	..	..	..
			2	U	U	..	..	..	..	..	Q	..	..	..
			3	U	U	Qa	Qa	Q	Q	U	U	..	..	..
			4	U	U	..	..	..	..	Q	Q	..	..	..
			5, 28	U	U	..	..	..	..	..	Q	..	..	..
			6	U	U	Q	Q	Q	Q	Q	Q	..	..	..
			7, 11	U	U	Q	Q	Q	Q	Q	U	..	..	..
			8, 9	U	U	Qa	Qa	Q	Q	Q	U	..	..	..
			10	U	U	U	U	U	U	U	U	Q	..	..
			12-17, 21-23, 25, 27	U	U	..	..	..	..	..	U	..	..	..
			18, 19	..	UL	..	..	..	..	..	Q	..	..	..
48	Adams	1461017	1-3, 13-15, 17	U	U	..	..	..	..	..	U	..	..	..
			4	..	..	..	..	..	..	..	Q	..	..	..
			5, 7-9	U	U	..	..	..	..	..	Q	..	..	..
			16, 20, 22	Q	Q	..	..	..	..	..	Q	..	..	..
			21	U	U	..	..	..	..	..	Q	..	..	..
49	Manley	1462143	7, 8	..	Q	..	..	..	..	..	U	..	..	..
50	Adams	1462677	32	..	..	..	..	..	..	..	Q	..	..	..
51	Adams	1464678	23	..	..	..	..	..	..	..	Q	..	..	..
53	Hall	1175909	9, 18	..	..	..	..	..	..	..	..	Q	..	..
56	Hall	1242795	1	..	..	..	..	..	..	..	..	Q	..	..
			3, 8, 9	..	..	Q	Q	Q	Q	Q	Q	Q	..	..
57	Hall	1242796	4, 16, 21	..	..	..	..	..	..	..	..	Q	..	..

[fol. 1152]

Gasoline Products Co. patents:

65	Cross	1423500	1-15	..	..	..	..	..	..	..	..	Q	Yes

Miscellaneous patents:

67	Chamberlain	1221790	1-25	..	..	Q	Q	Q	Q	..	..	..	..	..	..

Products patents:

70	Ellis	1318060	1-15	U	U	Q	Q	Q	Q	Q	..	..	..	..	..
71–75	Ellis	1318061		U	U	U	U	U	U	U	..	U	..	..	..
76	Burton	1167884		U	U	U	U	U	U	..	..	U	..	..	..

	Miscellaneous patents:												
67	Chamberlain	1221790	1-25			Q	Q	Q	Q				
	Products patents:												
70	Ellis	1318060	1-15	U	U	Q	Q	Q	Q	Q			
71–75	Ellis	1318061		U	U	U	U	U	U	U		U	
76	Burton	1167884		U	U	U	U	U	U			U	
77	Burton	1167884		Q	Q	U	U	U	U				
78	Burton	1167884		U	U	F, not now	F, not now	F, not now	F, not now	F not now			

NOTE.—This table omits all reference to the use of the Burton process by the Standard Oil Co. of New Jersey, inasmuch as the Burton process is the process of the Standard Oil Co. of Indiana; all reference to the use of the Hall process, which has been abandoned, and to the approval of licenses by the Texas Co., which is the same as the HM No. 1 and HM No. 2 columns combined.

The following patents and patent claims are omitted as not used by any defendant:

Lang pat. No. 954,575; Burton pat. No. 1,112 113; Humphrey and Burton pat. No. 1,343,674; Palmer pat. No. 1,313,009; Palmer pat. No. 1,360,973; Wells pats. Nos. 1,187,874, 1,232,545, 1,248,225; Ellis pats. Nos. 1,216,971, 1,249,278, 1,317,868, 1,341,-975, 1,396,999; Clarke pat. Nos. 1,405,286 and 1,413,899; Claims 1-8, 10-12, 21, 22, 25-28 of Adams pat. No. 1,320,354; Claims 1-5, 8-11 of Adams pat. No. 1,320,726; Claims 1, 3, 5, 8-24, 26, 27, 28 of Adams pat. No. 1,320,727; Adams pat. Nos. 1,428,311, 1,428,-312, 1,428,338, 1,445,281, 1,455,376, 1,455,377, 1,462,677, 1,462,678, 1,477,860, 1,506,877, 1,506,878; Claims 1-8 of Manley pat. No. 1,428,338; Manley pat. No. 1,428,339, Claims 1-6 of Manley pat. 1,462,143; Claims 1-8, 10-12, 14-17 of Hall pat. No. 1,175,909; Claims 1-8, 10, 16 of Hall pat. No. 1,175,910; Hall pat. 1,194,289; Claims 2, 4-7 of Hall pat. No. 1,242,895, Claims 1, 3, 5-15, 17, 18, 20, 22, 23, 24 of Hall pat. No. 1,242,796; Hall pat. 1,261,930; Claims 2 and 4 of De Florey pat. No. 1,437,045; Cross pat. No. 1,326,-851; Ellis pat. No. 1,396,999.

The following patent and patent claims are omitted because they are not used by any company except the company owning them:

Standard Oil Co. of Indiana patents	Burton No. 1,055,707; Humphreys pats. Nos. 1,122,002 and 1,122,003; Rogers & Cooke patent No, 1,122,220; Moore patent No. 1,130,318, Clarke patent No. 1,132,163.
Standard Oil Co. of N. J. patents	Claim 3 of Ellis pat. No. 1,415,232; Clarke et al. pat. No. 1,478,102.
Texas Co. patents	Claim 9 of Manley pat. No. 1,428,338; Claims 10, 11, 12, 18, 19 of Adams pat. No. 1,461,-017; Claim 13 of Hall pat. No. 1,175,909; Claims 9, 11-15, 17 of Hall pat. No. 1,175,-910; Claims 2, 19 of Hall pat. No. 1,242,796; Hall pat. No. 1,285,136.
Gasoline Products Co. patents	Claims 1, 3, 5, 6 of De Florez pat. No. 1,437,045. Cross pats. Nos. 1,203,312 and 1,437,229.
Miscellaneous patents	Clarke pat. No. 1,112,260; Hall pats. 1,239,099 and 1,239,100.

Patent used and abandoned by company other than its owner. Cash patent No. 1,230,065.

[fol. 1153] PETITIONER'S EXHIBIT 170

United States Patent Office

Carleton Ellis, of Montclair, New Jersey,, Assignor to Ellis-Foster Company, a Corporation of New Jersey

Motor-Spirit.

1,318,060. Specification of Letters Patent. Patented Oct. 7, 1919

No Drawing. Original application filed August 21, 1913. Serial No. 785,855. Renewed December 12, 1918. Serial No. 266,512. Divided and this application filed October 12, 1917. Serial No. 196,204.

To all whom it may concern:

Be it known that I, Carleton Ellis, a citizen of the United States, and a resident of Montclair, in the county of Essex and State of New Jersey, have invented certain new and useful improvements in Motor-Spirits, of which the following is a specification.

This invention relates to a petroleum product suitable for use in automobile engines and the like, and relates in particular to a motor spirit of gasolene-like material which may be obtained through the pyrogenetic decomposition or cracking of kerosene or heavier oils and other treatment as will be hereinafter illustratively described. This application is divided from my co-pending application Serial No. 785,855 renewed Serial No. 266,512.

In producing one form of the product comprised under the present invention I may start with a petroleum oil, say, kerosene, which may have a gravity of 42° Bé. or thereabout. This may be passed through a heated conduit, as for example, an iron pipe of a length preferably 50—100 feet, which pipe is preferably heated to around 425 to 480° C. and in some cases may be packed loosely with suitable contacting material such as nickel plated fragments of iron of irregular shape. Also in some cases water may be introduced with the kerosene or other oil, if desired, although tending to somewhat retard the splitting operation, but on the other hand, sometimes having a favorable influence on

the character of the resulting product. Five per cent. of water calculated on the amount of oil introduced, is usually a satisfactory proportion. As stated, the use of water is optional.

The product emanating from the conduit forming the heating zone consists of fractions which on the one hand are lighter than the kerosene or the oil employed and on the other hand contain heavier products probably due to polymerization during the treatment. Very curiously these are oftentimes so proportioned that the specific gravity of the light oil counterbalances that of the heavier oil formed and the mixed distillate may thus show approximately the same specific gravity as the original kerosene or similar oil. For instance, a 42° gravity kerosene may give a product of almost precisely this gravity or perhaps 42.5 or 43° Bé. which may contain 30% or so of gasoline-like material.

The product obtained by this pyrogenetic treatment is separated into lighter and heavier parts by fractional condensation which may be followed, if desired, by fractional distillation and a gasolene fraction boiling to 125° C. or 150° C. obtained. This fraction is usually of brown color and of disagreeable odor.

When one attempts to refine it in the ordinary way using concentrated sulfuric acid followed by alkali, the gasolene tends to blacken or darken through formation of a relatively large amount of tar or coke-like material and this discoloration is not easily removed by water and alkali. In oil refining operations, so objectionable is the diluting effect of any water which may be present in the oil on the strong acid used that it has been recommended, for example, to very carefully dry the oil prior to the actual acid refining step. With cracked raw material of the present process this is not desirable unless, of course, excessive amounts of water be accidentally present. In the treatment of cracked gasolene, containing a substantial proportion of unsaturated bodies, I have found that acid which is more or less diluted with water acts more satisfactorily than the concentrated acid, which is contrary to expectations. Acid of 40.70% strength of sulfuric anhydrid causes a better and more satisfactory conversion of the unsaturated material.

An illustrative example will serve to make this clear. Kerosene of 42° Bé. was run through a tube of suitable length heated to such a temperature that the escaping oil vapors were maintained at a temperature about 465° C. which required a temperature about the tube of approximately 630° C. The vapors were passed through an air condenser then through a water condenser and finally the gases escaping from the latter were bubbled through heavy oil in order to remove some of the entrained condensable material. A portion of the condensate was distilled and cut at 105° C. and a fraction of gasolene-like material having a gravity of 55° B. was obtained which amounted to 25% [fol. 1154] of the total condensate taken for distillation. When the same condensate was cut at 140° C. instead of 105° C. the fraction obtained amounted to 27% and had a gravity of 54.5° B. Similarly when a third portion of the condensate was cut at 150° C. a fraction amounting to 32% of the original condensate was obtained and the gravity of this material was 53° B. The residue in the retort had a gravity of approximately 38° Bé. From the heavy washing oil through which the gases from the cracking stage were bubbled as described above a further yield of gasolene-like material was obtained.

The gravity of the product as drawn from the heated tube was 43° Bé, or only one degree lighter than the original kerosene. On exposing the fraction distilling over below 100° C. to air in an open dish, the major proportion of the material evaporated leaving a thick greasy material of whitish color resembling very soft vaseline. On very careful distillation of the crude gasoline or on passing air through the latter a similar product was formed which separated to some extent from the volatile hydrocarbons.

The thick greasy material referred to in the specific illustrative example set forth above, which may for convenience be called polymer "A," and which probably was a product of polymerization and oxidation, in the particular case noted above, decomposed when heated, vapor being given off at 110° C. and a transformation accompanied by a slight or mild explosion taking place at 125° C. This applies to the separated polymer "A," obtained as described, as in solution in the hydrocarbon, the heating may be carried up to 160° C. or so, without explosion, but usually with the dis-

engagement of some gas. When polymer A is heated to 125° C. the reaction which takes place causes the formation of considerable gas and the production of a brownish liquid of somewhat thinner consistency than polymer "A."

A quantity of the crude spirit obtained in this illustrative manner and which distilled up to 150° C. in an ordinary distilling apparatus was fractionated with a rectifying column and the following fractions were obtained:

Fractions	Percentage by volume	Iodin number
No. 1, up to 70° C.	9	310
No. 2, 70-85° C.	8.4	233
No. 3, 85-100° C.	8.6	218
No. 4, 100-115° C.	9.2	168
No. 5, 115-130° C.	8	136
No. 6, 130-150° C.	14	87.8
No. 7, above 150° C.	19	53

The color of the different fractions above tabulated varied from practically colorless in number 1, nearly colorless in numbers 2 and 3, slightly darker in number 3 and 4, progressively to rather dark brown products in fractions 6 and 7. All the fractions ignited easily in an open dish at room temperature except fraction 7 which ignited but not as readily. When these fractions are burned in open dishes a resinous-like residue forms in some of them, the largest amount being present in fractions 2 and 3, boiling between 70 and 100° C. The formation of this resinous body may be ascribed to the presence of polymer "A" and may be eliminated by suitable hydrogenation, but with great difficulty by distillation.

The formation of these resinous or sticky materials in the carburetors of an internal combustion engine of course soon cause trouble.

When agitated with about 5% of sulfuric acid of 50% strength, the acid quickly turns a deep brown, but the motor spirit remains clear, or at the most is only tinted a yellow color. After agitation in this manner, the acid is removed by washing with water and, for example, about 5% of caustic soda solution of 20° Bé. is introduced and the hydrocarbon agitated for a time until reaction is complete;

then the product is washed thoroughly with water to remove the alkali.

A quantity of this material passed through a carbureter which previously has been weighed was found to leave the apparatus free from resinous traces and any residue, if present, was negligible in amount.

The foregoing illustrates the results obtained with one sample of oil under certain conditions and, of course, considerable variations arise with changes in temperature, pressure and nature of the raw materials yielding a variety of products falling within the range of my invention.

The above mentioned residue left in the retort in the practice of the process and having a gravity of 38° Bé. when passed through a heated tube under approximately the same conditions, gave a yield of gasolene-like material of which 26%, or thereabout, was obtained by distilling up to 150° C. This is somewhat less than the percentage of gasolene-like material obtained from the first running using the original kerosene of 42° Bé., in which case over 30% of gasolene-like material distilling up to 150° C. was secured.

By the term gasolene-like material I do not wish it to be inferred that the product derived in this manner is exactly like gasolene chemically, because ordinary or natural gasolene is either entirely saturated or shows a very slight iodin absorption and may be refined with sulfuric acid of full strength. The iodin number of the raw or crude low- [fol. 1155] boiling gasolene-like material obtained by this method before treatment with sulfuric acid may in some cases range around 100 to 150 and for certain fractions these may run much higher as indicated above.

Instead of using sulfuric acid under conditions to produce strict sulfonation and tar formation which takes place when the acid is highly concentrated, I preferably in accordance with the present invention use an acid which has been diluted with water or other diluting medium so that the strength is lowered, as for example, to 40—60% or 70% as previously noted, although this percentage may be higher or lower depending on the iodin number of the oil, as well as on its other characteristics and the foregoing is merely set forth in an illustrative sense and I do not wish to be limited to any disclosure of precise procedure as laid

down herein, but wish to embrace such equivalent methods of treatment or range of treatment as fall within the scope hereof.

After treating the crude product with sulfuric acid of say 50% strength, a stronger acid may follow as the more readily charred bodies may be removed by the more dilute acid and further extraction and refining by stronger acid as 60, 70, or 80% strength may then be brought about. Oxidizing agents such as a somewhat dilute solution of chromic acid may be used to improve the color. Filtration or other suitable contact with charcoal also is useful.

The strength of the sulfuric acid to be employed in producing the product of this invention in its preferred aspects may be conveniently found in a practical manner by treating a series of samples of the spirit obtained from the cracking step with acid of different strengths ranging from about 40% and upward. If a determination of the iodin number is first made to indicate the degree of unsaturation, the effect of sulfuric acid may be ascertained in one of two ways. Either the start may be made with strong concentrated (anhydrous) acid and then progressively diluted acid used until the correct reaction strength is found, or 40% acid may be used at the start and acid of progressively increasing strength employed until the correct reaction strength is found, by this procedure. With cracked material of an iodin number of between 200 and 300 the latter method is best as the more dilute acid is likely to prove the correct reagent for permanent use. With iodin numbers below 100 the former method is recommended. If the strength of the acid is too great for desirable practical operation, especially with the products of high iodin numbers, charring or vigorous carbonization will occur and in such cases the cracked material collecting above the sulfuric acid layer after such treatment is usually discolored to such an extent as to be unsatisfactory in appearance as a commercial article while in the acid layer are frequently found carbonized masses usually discolored to such an extent as to be unsatisfactory in appearance as a commercial article while in the acid layer are frequently found highly carbonized masses.

With the preferred strength of acid as found in this manner, the upper layer of hydrocarbon is normally of a

relatively light color and any coloration present is usually fairly well removed by treatment with alkali and washing. When an acid of a strength substantially not permanently discoloring the hydrocarbon has thus been ascertained, such strength of acid may be regularly used in large scale operation under approximately the same conditions, over an indefinite period. Of course slight variations from day to day in the cracked product do not require readjustment of conditions. Once the proper strength of acid is found for the manner of operation in hand no change is usually required over long periods. A slightly larger or smaller proportion of olefins or other unsaturated bodies in the crude cracked spirit does not necessarily call for the modification of the strength of the acid as some latitude in this respect is feasible. A light colored or water-white gasoline is prepared with difficulty from cracked oil running high in readily oxidizable olefins if too concentrated an acid is employed as usually some coloring matter forms which is soluble in the gasolene and which is not readily extracted by alkali and which can be removed by bleaching agents only at considerable expense. Consequently to prepare a clear substantially water-white gasolene free from such discoloring agents, the strength of the acid may be adjusted as indicated in the foregoing so that carbonization will be so slight as not to bring about the objectionable formation of gasolene soluble dyestuffs and the adjustment of the acid to this strength for any given grade of cracked material may be made with small samples first until the desired strength of the acid is found for the particular grade of cracked material under treatment.

Ordinary natural gasoline, as stated, has a low iodin absorption or none at all, while the present product, it will be noted, normally has a relatively high iodin number. In spite of this, the aforesaid treatment renders the product relatively stable. Moreover, generally speaking, it is more volatile than ordinary gasolene. In fact the new product having in one instance, a gravity of say 52° Bé. apparently operates in carburetters equally as well as, or better than [fol. 1156] common gasolene of about 54° or 55° Bé. The unsaturated condition of the new product apparently renders it more reactive with oxygen enabling greater ease of

ignition and more uniform explosion in internal combustion engines.

At a gravity of say, 54°, Bé., for both common gasolene and the preferred product of the present invention, the latter in its preferred form shows greater volatility, diffuses more easily, has a lower flash point and is ignited with greater ease and seemingly is burned more effectively than the former. It appears that a considerable degree of unsaturation is not undesirable if the gasolene has been extracted by acid of predetermined strength as above indicated, as smooth engine operation may be maintained by the use of products of this character. The olefins, etc., which may remain after such extraction, although stable enough to be relatively permanent in storage, are yet apparently sufficiently sensitive to aid in the responsiveness of the fuel when used in internal combustion engines.

My product in its preferred aspects has an iodin number not less than 30, but preferably is higher and even may be in excess of 75 or 100, under some circumstances, and in its preferred form is substantially free from olefins readily forming resinous bodies on exposure to air.

The foregoing description is given in detail but it is to be understood that such illustrative matter is not to be construed as a limitation defining the invention in any narrower sense than is comprehended by the substance of the appended claims.

Thus in the operation of the foregoing process to yield a preferred form of the product involved in the present invention, heavier hydrocarbon material is exposed to a cracking temperature, as for example, by passage of said material through a heated zone to effect decomposition, and the products of such decomposition, particularly the lighter fractions, are subjected to the action of an acid comprising sulfuric acid of predetermined strength; whereby easily oxidizable or attackable olefins are extracted and in adjusting the strength of the acid to suitably extract these or other olefin bodies which are to be removed, employing further extraction with stronger acid if required to remove olefins not extracted by the weaker acid; and my invention thus embraces as the preferred form of the present invention a gasolene substitute or motor spirit consisting of, or comprising cracked gasolene

material, that is, gasolene material made by heat decomposition of a heavier oil preferably substantially freed from olefin or kindred bodies of an easily oxidizable or resin-forming character yet containing some unsaturated bodies, and in the preferred form exhibiting an iodin absorption value or number of 30 or over, while preferably or ordinarily having a flash point lower than normal natural gasolene of corresponding specific gravity.

What I claim is:

1. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies and having greater volatility than gasolene of corresponding specific gravity.

2. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies corresponding to an iodin number of at least 30 and having greater volatility than gasolene of corresponding specific gravity.

3. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies corresponding to an iodin number of about 75 and having greater volatility than gasolene of corresponding specific gravity.

4. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies but being substantially free from unsaturated bodies readily forming resinous bodies upon exposure to air.

5. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies corresponding to an iodin number of at least 30 but being substantially free from unsaturated bodies readily forming resinous bodies upon exposure to air.

6. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies corresponding to an iodin number of about 75 but being substantially free from unsaturated bodies readily forming resinous bodies upon exposure to air.

7. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies, having greater volatility than gasolene of corresponding specific gravity and being substantially free from unsaturated bodies readily forming resinous bodies upon exposure to air.

8. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies of the aliphatic series.

9. The herein described motor spirit consisting of gasolene like material of a complex character containing a sub- [fol. 1157] stantial amount of unsaturated bodies of the aliphatic series, corresponding to an iodin number of at least 30.

10. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies of the aliphatic series corresponding to an iodin number of about 75.

11. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies of the aliphatic series but being substantially free from resinifying olefins.

12. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of unsaturated bodies of the aliphatic series corresponding to an iodin number of about 75 but being substantially free free from resinifying olefines.

13. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of stable unsaturated bodies.

14. The herein described motor spirit consisting of gasolene like material of a complex character containing a substantial amount of stable unsaturated bodies and substantially free from resinifying olefins.

15. The herein described motor spirit of a complex character and substantially water-white color consisting of gasolene like material of a complex character containing a major portion of saturated petroleum hydrocarbons and

a substantial amount of relatively stable olefins but being substantially free from olefins readily forming resinous bodies on exposure to air.

Carleton Ellis.

[fol. 1158] PETITIONER'S EXHIBIT 171

United States Patent Office

William M. Burton, of Chicago, Illinois, Assignor to Standard Oil Company, of Whiting, Indiana, a Corporation of Indiana

Petroleum Product

1,167,884. Specification of Letters Patent. Patented Jan. 11, 1916

No. Drawing. Application filed February 20, 1915. Serial No. 9,754

To all whom it may concern:

Be it known that I, William M. Burton, a citizen of the United States, residing at Chicago, in the county of Cook and State of Illinois, have invented a new and useful Improvement in Petroleum Products, of which the following is a specification.

My invention relates to improvements in petroleum products.

More particularly the invention has reference to certain new products which are obtained from the liquid residue of petroleum distillation as carried out according to the processes described in my prior Patents No. 1,049,667 dated January 7, 1913 and No. 1,105,961 dated August 14, 1914.

In the first of my prior patents above referred to a distillation process is disclosed which consists in brief of the following procedure: High-boiling point hydrocarbons, (i. e., hydrocarbons having a boiling point upward of 500° F., mainly of the paraffin series, and known under the trade terms of fuel oil or gas oil, are distilled at a temperature of about 750° F. and under a pressure of upward of three atmospheres, this pressure being maintained not only on the contents of the still but throughout the course of the resulting vapors up to and during their condensation. In such

distilling operation approximately sixty to seventy per cent of the contents of the still will be driven off in one run, i. e., in a period of about thirty-six hours, at the end of which period the fires may be drawn and the liquid residue, consisting of about thirty to forty per cent of the original charge, may be permitted to cool and then drawn off, the still being thus emptied for the purposes of cleaning preparatory to beginning another run.

In the second of my patents referred to above I disclose a process by which this thirty to forty per cent residue which is withdrawn from the pressure still at the end of a run of the latter may be prepared for a second treatment according to the process of my first patent above referred to. Very briefly, it may be stated that according to the process of my second patent, the thirty to forty per cent residue withdrawn from the pressure still is led to a second still and in this last still is distilled down to dryness under atmospheric, or approximately atmospheric, pressure, the distilled vapors being condensed in a water-condenser and led to a receiving drum. In this process about 95% of the contents of the still will go over to the condenser and drain into the receiving drum, the remaining 5% appearing as coke or carbon in the still. According to the process of my Patent No. 1,105,961 the liquid collected in the receiving drum was again subjected to the pressure distillation process of my Patent No. 1,049,667, either alone or mixed with a fresh charge of fuel oil or "bottoms" from the re-distillation of crude gasolene, the end and aim of the processes of both my prior patents referred to being the production of a maximum quantity of the low-boiling point hydrocarbons known as gasolene.

I have recently discovered, however, that the distillate from the thirty to forty per cent, residue remaining in my pressure still at the end of a run of the latter, and which as disclosed in my prior Patent No. 1,105,961 I formerly again subjected to the pressure distillation process and thereby converted into gasolene, is itself a new and useful petroleum product, having valuable properties not found in any other petroleum product heretofore known and being readily distinguished from all other products by simple physical tests.

My new petroleum product as made by the process above described consists of a mixture of oils of varying specific

gravity and chemical composition, in large part members of the upper range of the paraffin series, but including also some proportion of unsaturated hydrocarbons, asphalts, cyclic compounds and other products and by-products of petroleum distillation, the exact constitution of my oil being dependent upon the nature of the raw material used in its manufacture. That is, it will be understood that the fuel oil or gas oil which forms the raw material from which my new product is made is itself a mixture of the various residues of petroleum distillation and may vary to a considerable extent in chemical composition, according to the relative proportions of the various residual oils. Being obtained from such a raw material, my new product naturally is subject to certain minor variations in its chemical constitution, but, as before stated, it may be said to con- [fol. 1159] sist largely of members of the upper range of the paraffin series. The salient characteristic of my new product, and that which distinguishes it most readily from all previously known petroleum oils, is its exceedingly low viscosity. I find that a typical series of fractions of my new product, taken from the still at intervals during a run of the latter will show the following relations between the gravity and viscosity of the fractions:

Baumé gravity	Viscosity at 100° (Saybolt viscosimeter)
28.9	36
26.5	38
23.8	42
21.5	45
21.1	51
20.2	52
18.7	58
17.8	62
17.2	65
16.7	66
15.8	76
15.2	88
15.0	89
14.7	97
14.1	105
13.2	110
13.0	116
12.0	158
10.8	198

For purposes of comparison I will also set forth similar gravity-viscosity tables of some common petroleum oils made by other processes:

Oils made from California Crude Petroleum

Gravity	Viscosity at 100°
18.8	449
20.4	235
20.6	339
21.6	146
21.8	167
22.5	139

Oils made from Kansas-Oklahoma Crude Petroleum

Gravity	Viscosity at 100°
25.0	235
26.0	190
26.0	165
26.5	145
27.5	100

By plotting graphically the gravity-viscosity curve of the fractions which make up my new product, and by plotting similar gravity-viscosity curves of the other oils given by way of example it will be clearly seen that over the whole range of its constituent fractions my product has a considerable lower viscosity than other oils of the same gravity or density. This difference is so marked as to be readily distinguishable by even the most approximate tests, and my new product has, because of its most unusual properties in this respect, displaced other products in commercial uses in which a heavy oil having a low viscosity is desired.

In physical appearance and in chemical constitution my new product appears to be substantially the same as other petroleum oils of the same gravity. It may be filtered, treated with acids and alkalis, fractionated and otherwise subjected to the customary processes of petroleum refining in so far as is necessary to fit it for any particular use, retaining always, however, to a marked and clearly distinguishable degree, the salient novel characteristic pointed out, that is, an exceedingly low viscosity relative to its gravity.

As has been pointed out in the foregoing specification, my new product is not a single oil of definite chemical composition, but a mixture of oils, largely of the saturated or paraffin series but varying considerable in specific gravity and capable of being fractionated or otherwise separated into its constituents parts, or into mixtures of any of these constituents, according to the use to which it is to be put. For example, the heavier fractions have been found particularly useful as an impregnating agent for binder twine, a preferred oil for this purpose being a mixture having a gravity of about 15° Baumé and a viscosity at 100° F. of about 135 (Saybolt), the mixture comprising fractions ranging in gravity from about 10° to 20° and in viscosity from about 200 to 50. For other purposes heavier or lighter fractions or various mixtures of the same may be employed to obtain a mixed product of the desired gravity, and such product, regardless of its exact constitution, will in all cases be clearly distinguished from all products heretofore known by reason of its low viscosity.

The exact physical and chemical properties of the oils which constitute my new product may obviously vary through quite a wide range and for the purpose of defining my product, I shall, therefore, refer only to its salient, novel characteristic which will in every case be sufficient to distinguish it from all petroleum products heretofore known. For the purpose of best defining this relation between gravity and viscosity which distinguishes my product, I find it convenient to plot a gravity-viscosity curve in rectangular coördinates. This curve I find to be in general form a conic section, the approximate equation of which is

$$.51x^2+106xy-961x-29y^2-244y-53296=0,$$

where "x" is the viscosity at 100° F. as measured by the Saybolt viscosimeter and "y" is the Baumé gravity of the oil.

While the mathematical curve as expressed by the foregoing equation does not follow absolutely the actual relation between gravity and viscosity of the various oils which constitute my new product, it expresses this relationship within a fair degree of accuracy and sufficiently closely to

identify my product and to distinguish it clearly from all other petroleum oils.

What I claim is:

1. As a new article of manufacture, a petroleum oil characterized by the following approximate relation between its [fol. 1160] gravity and its viscosity:

$$.51x^2+106xy-961x-29y^2-244y-53296=0,$$

where "x" is the viscosity at 100° F. according to the Saybolt viscosimeter and "y" the Baumé gravity of the oil.

2. As a new article of manufacture, a petroleum distillate produced by the following process: distilling an oil having a boiling point of upward of 500° F. at a temperature from about 650° to 850° F. and under a pressure of upward of three atmospheres until about 65% of the oil has been distilled over, drawing off the residue from the pressure still, distilling the latter under approximately atmospheric pressure, and condensing and collecting the distillate.

3. As a new article of manufacture, a petroleum oil having a Baumé gravity of approximately 15° and a viscosity of approximately 130°, as measured by the Saybolt viscosimeter at 100° F. and comprising a mixture of fractions mainly of the paraffin series and having a Baumé gravity varying approximately from 20° to 10° and a corresponding viscosity ranging approximately from 50 to 200.

William M. Burton.

In presence of L. Heislar, D. C. Thorsen.

[fol. 1161]

PETITIONER'S EXHIBIT 174

W. M. BURTON.

MANUFACTURE OF GASOLENE.

APPLICATION FILED AUG. 25, 1913 RENEWED MAY 25, 1914.

1,105,961. Patented Aug. 4, 1914.

2 SHEETS-SHEET 1

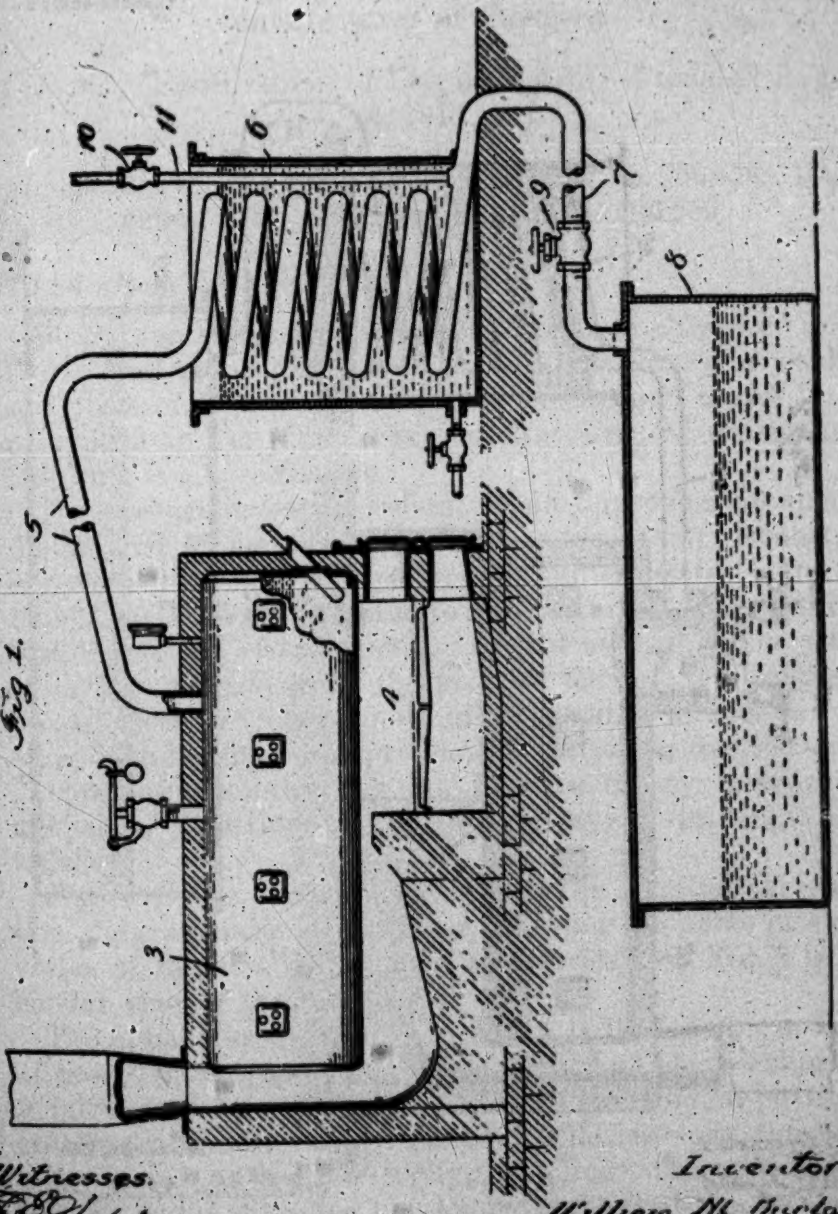


Fig 1.

Witnesses.
C. E. Clayford
Geo. H. Bissell

Inventor
William M. Burton
By Dyrenforth, Lee, Chritton & Wales
Atty's

Pe 174-1

4452

[fol. 1162]

W. M. BURTON.

MANUFACTURE OF GASOLENE.

APPLICATION FILED AUG. 25, 1913. RENEWED MAY 28, 1914.

1,105,961.

Patented Aug. 4, 1914.

2 SHEETS—SHEET 2.

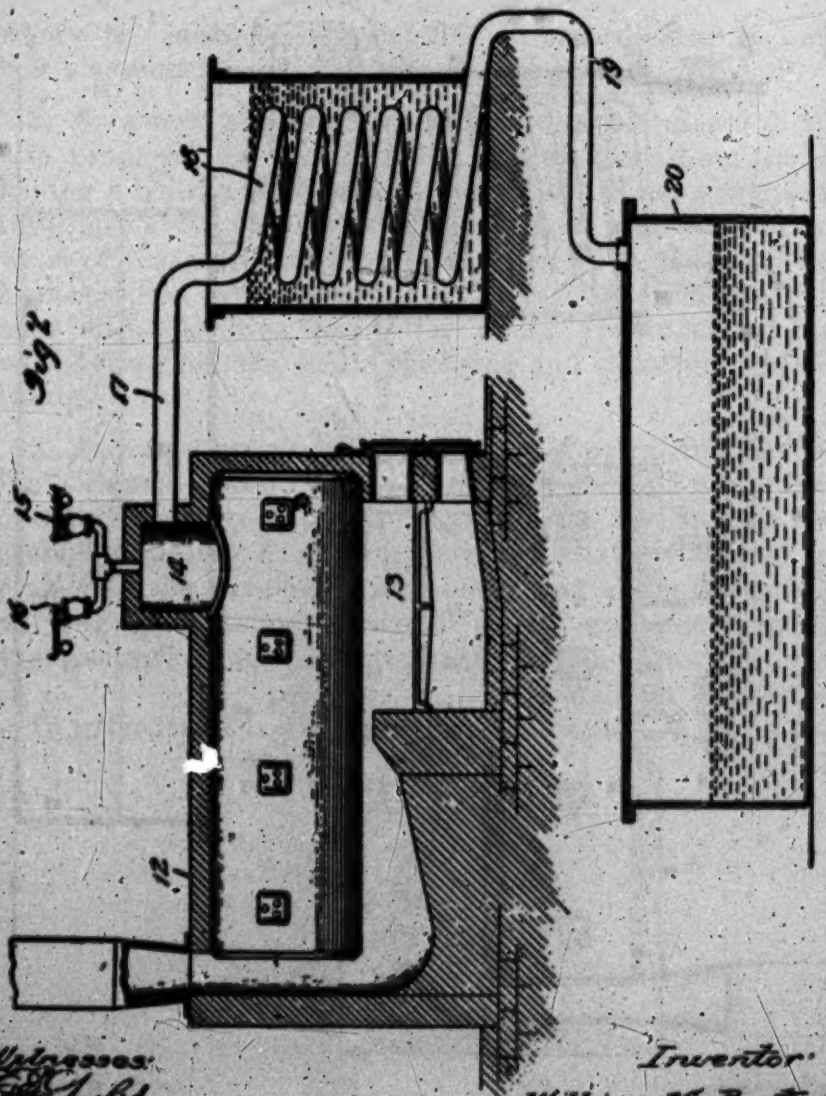


Fig 2

Witnesses:

Inventor:
William M. Burton.
By Dyrenforth, Lee, Chris... Wiles & Allyn.

PX174-2

[fol. 1163] United States Patent Office

William M. Burton, of Chicago, Illinois, Assignor to Standard Oil Company, of Whiting, Indiana, a Corporation of Indiana

Manufacturer of Gasolene

1,105,961. Specification of Letters Patent. Patented Aug. 4, 1914

Application Filed August 25, 1913. Serial No. 786,456. Renewed May 25, 1914. Serial No. 840,959

To all whom it may concern:

Be it known that I, William M. Burton, a citizen of the United States, residing at Chicago, in the county of Cook and State of Illinois, have invented a new and useful Improvement in the Manufacture of Gasolene, of which the following is a specification.

The present invention relates to an improvement upon the method of manufacturing low boiling point products of petroleum-distillation set forth in United States Letters Patent No. 1,049,667, granted to me January 7, 1913; and it is in the nature of an extension of that method, to the end of greatly increasing, by the practice thereof, the production of these products from a given quantity of fuel-oil or other high-boiling-point product of petroleum distillation.

Apparatus suitable for the practice of my improved method is illustrated in the accompanying drawings, in which—

Figure 1 is a broken view in vertical longitudinal section, diagrammatic in character, showing the parts in elevation of the first still and its accessories, and Fig. 2 is a similar view of the second still.

The apparatus illustrated in Fig. 1 is that shown in the aforesaid patent, according to the method of which a supply is introduced into the still 3 of the residual liquid-portion of the paraffin-series of petroleum-distillation—say, the distillate known as fuel oil—having a boiling point upward of 500° F., and is subjected to a temperature from the furnace 4, of about 650° F. to about 850° F. to distil its volatile constituents, which are conducted off by a pipe 5 through a con-

denser 6, the coil of which discharges through a pipe-extension 7 into a receiver 8 for the products of condensation. In this pipe-extension, and thus beyond the discharge-end of the coil, is contained a normally-closed shut-off valve 9 for maintaining a pressure of from about 4 to 5 atmospheres on the liquid in the still of the vapors throughout their course to and through the condenser; and this pressure of the vapors combined with their contained heat converts the high boiling point members of the paraffin series into low boiling point members of the same series. This method of distillation is continued until the residue in the still is reduced to a thin syrup-like consistency, and the original charge has been reduced to from 30 to 40 per cent of its bulk. In the meantime, it is desirable to open, from time to time, a relief-valve 10 in the upper end of a pipe 11 rising from near the lower end of the condenser-coil, for relieving the gas-pressure, which is liable to accumulate in the coil and obstruct the action of the apparatus.

It is at this point that my present improvement begins: The residue is withdrawn from the still 3 and is introduced into a second still 12, heated by a furnace 13 and provided with a vapor-dome 14 equipped with a pressure safety-valve 15 and a vacuum safety-valve 16, both of which are of well-known construction and manner of operation, and need not, therefore, be shown nor described in detail. A pipe 17 connects the vapor-dome with a condenser-coil 18, discharging from its lower end through an extension 19 into a receiver 20.

The contents of the still are maintained under atmospheric or approximately atmospheric pressure thereon while under subjection to heat from the furnace 13, to distil the volatile constituents of said contents, which are conducted off through the pipe 17 and condensed in the condenser; and the products of condensation accumulate as a yellowish liquid in the receiver 20. This procedure is carried on until the original contents of the still 12 have been reduced to a condition of dryness, the distillate accumulated in the receiver 20 amounting to about 95 per cent of the charge in the still 12.

The liquid of condensation in the receiver 20 is withdrawn therefrom and introduced into the still 3, or into another like it for separate treatment, and is there sub-

jected to the original process described as being practised therein; and the resultant distillate is a low boiling point product, belonging to the paraffin series, the same as the second petroleum residue from which it was distilled. It is my practice, and the preferable one, instead of treating the contents of the receiver 20 separately in a still 3, as suggested, to mix them with original residue treated therein; though the result is the same in either case. By following the last-named practice, about 63½ per cent of the original charge in still 3 is converted into gasolene, about 1½ per cent going off in the form of gas, which I use as fuel for [fol. 1164] heating that still. This leaves somewhat less than 35 per cent of the original charge as residue to be treated in still 12, from which about 95 per cent is distilled, leaving about 5 per cent as dry residue or coke; and this distillate being turned back into still 3 for treatment with the charge introduced therein for the original treatment again produces in the first still the same yields of about 63½ per cent of gasolene and about 35 per cent of residue. In this way the practice may be carried on endlessly, by the addition of fresh charges into the high-pressure still 3.

I thus succeed in converting practically all (not considering the incidental losses) of the original high boiling point product first treated by the process practised in still 3 with its described accessories, into a superior article of gasolene of the same paraffin series or group as that of the aforesaid original residue.

It will, of course, be understood by those skilled in the art, that the low-boiling point product herein referred to as gasolene, is crude gasolene, which has to be prepared for the market by first treating it with strong sulfuric acid and then re-distilled to produce the finished deodorized gasolene, and that the sulfuric-acid treatment entails a loss of about 1¼ per cent; also the so-called "bottoms" are left over from the re-distillation. However, it is my practice to introduce these bottoms into the still 3 and mix them with the materials treated therein.

What I claim as new and desire to secure by Letters Patent is—

1. The method of treating the liquid-portions of the paraffin-series of petroleum-distillation having a boiling

point of upward of 500° F. to obtain therefrom low-boiling-point products of the same series, which consists in distilling at a temperature of from about 650° F. to about 850° F. the volatile constituents of said liquid, conducting off and condensing said constituents, and maintaining a pressure of from about 4 to about 5 atmospheres on said liquid of said vapors distilling under approximately atmospheric pressure the volatile constituents of the residue of said first distillation and conducting off and condensing said last-named constituents, and finally subjecting the last product of condensation to the first-named treatment.

2. The method of treating the liquid-portions of the paraffin-series of petroleum-distillation having a boiling point of upward of 500° F. to obtain therefrom low-boiling-point products of the same series, which consists in distilling at a temperature of from about 650° F. to about 850° F. the volatile constituents of said liquid, conducting off and condensing said constituents, and maintaining a pressure of from about 4 to about 5 atmospheres on said liquid of said vapors throughout their course to and while undergoing condensation, distilling under approximately atmospheric temperature the volatile constituents of the residue of said first distillation and conducting off and condensing said last-named constituents, mixing this distillate with more of said liquid and subjecting it therewith to said first-named treatment.

William M. Burton.

In presence of L. Holzhalb, O. C. Avisus.

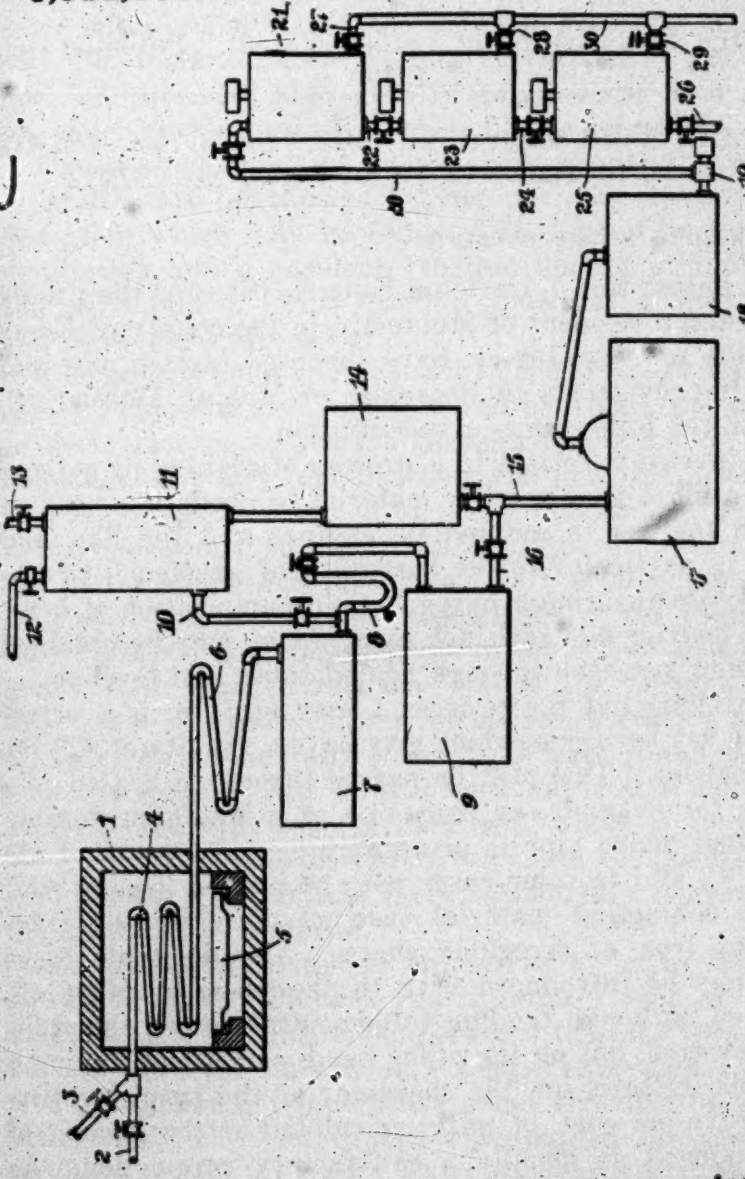
[fol. 1165] PETITIONER'S EXHIBIT 175

C. ELLIS.

PROCESS OF MAKING MOTOR FUEL.

APPLICATION FILED AUG. 21, 1913. RENEWED DEC. 12, 1918.

1,318,061. Patented Oct. 7, 1919.



Inventor:

Carleton Ellis

[fol. 1166] United States Patent Office

Carleton Ellis, of Montclair, New Jersey, Assignor to Ellis-Foster Company, a Corporation of New Jersey

Process of Making Motor-Fuel

1,318,061. Specification of Letters Patent. Patented Oct. 7, 1919

Application Filed August 21, 1913. Serial No. 785,855. Renewed December 12, 1918. Serial No. 266,512

To all whom it may concern:

Be it known that I, Carleton Ellis, a citizen of the United States, and a resident of Montclair, in the county of Essex and State of New Jersey, have invented certain new and useful Improvements in Processes of Making Motor-Fuel, of which the following is a specification.

This invention relates to a process of making or making and treating a gasolene-like material to produce a product suitable for use in automobile engines and the like, and relates in particular to the treatment of gasolene-like material obtained through pyrogenetic decomposition of kerosene or heavier oils such, for example, as may be obtained by passing kerosene through heated tubes and the like.

In carrying out my process I may start with a petroleum oil, say kerosene, which may have a gravity of 42° Bé. or thereabout. This may be passed through a heated conduit, as for example, an iron pipe of a length preferably 50-100 feet which pipe is preferably heated to around 425 or 480° C. and in some cases may be packed loosely with suitable contacting material such as nickel plated fragments of iron of irregular shape. Also in some cases water may be introduced with the kerosene or other oil, if desired, although tending to somewhat retard the splitting operation, but on the other hand, sometimes having a favorable influence on the character of the resulting product. Five per cent. of water calculated on the amount of oil introduced, is usually a satisfactory proportion. As stated, the use of water is optional.

The product emanating from the conduit forming the heating zone consists of fractions which on the one hand

are lighter than the kerosene or the oil employed and on the other hand contain heavier products due to polymerization during the treatment. Very curiously these are oftentimes so proportioned that the specific gravity of the light oil counter-balances that of the heavier oil formed and the mixed distillate may thus show approximately the same specific gravity as the original kerosene or similar oil. For instance, a 42° gravity kerosene may give a product of precisely this gravity or perhaps 42.5 or 43° Bé. which may contain 30% or so of gasolene-like material.

The product obtained by this pyrogenetic treatment is separated into lighter and heavier parts by fractional condensation which may be followed if desired by fractional distillation and a gasolene fraction boiling to 125° C. or 150° C. obtained. This fraction is usually of brown color and of disagreeable odor.

When one attempts to refine it in the ordinary way using concentrated sulfuric acid followed by alkali, the gasolene tends to blacken or darken through formation of a large amount of tar and coke-like material and this discoloration is not easily removed by water and alkali. In oil refining operations, so objectionable is the diluting effect of any water which may be present in the oil on the strong acid used that it has been recommended, for example, to very carefully dry the oil prior to the actual acid refining step. With cracked raw material of the present process this is not desirable, unless, of course, excessive amounts of water be accidentally present. I have found that acid which is more or less diluted with water acts more satisfactorily than the concentrated acid, which is contrary to expectations. Acid of 40-70% strength of sulfuric anhydrid causes a better and more satisfactory conversion of the unsaturated material.

An illustrative example will serve to make this clear. Kerosene of 42° Bé. was run through a tube of suitable length heated to such a temperature that the escaping oil vapors were maintained at a temperature about 465° C. which required a temperature about the tube of approximately 630° C. The vapors were passed through an air condenser, then through a water condenser and finally the gases escaping from the latter were bubbled through heavy oil in order to remove some of the entrained condensable

material. A portion of the condensate was distilled and cut at 105° C. and a fraction of gasolene-like material having a gravity of 55 Bé. was obtained which amounted to 25% of the total condensate taken for distillation. When the same condensate was cut at 140° C. instead of 105° C. the fraction obtained amounted to 27% and had a gravity of 54.5 ° Bé. Similarly when a third portion of the condensate was cut at 150° C. a fraction amounting to 32% of the original condensate was obtained and the gravity of this material was 53° Bé. The residue in the retort had a gravity of approximately 38° Bé. From [fol. 1167] the heavy washing oil through which the gases from the cracking stage were bubbled as described above a further yield of gasolene-like material was obtained.

The gravity of the product as drawn from the heated tube was 43° Bé., or only one degree lighter than the original kerosene. On exposing the fraction distilling over below 100° C. to air in an open dish, the major proportion of the material evaporated leaving a thick greasy material of whitish color resembling very soft vaseline. On very careful distillation of the crude gasolene, or on passing air through the latter a similar product was formed which separated to some extent from the volatile hydrocarbons.

The thick greasy material referred to above, which may for convenience be called "polymer A," and which probably was a product of polymerization and oxidation, decomposed when heated, vapor being given off at 110° C. and a mild explosion taking place at 125° C. This applies to the separated polymer A as in solution in the hydrocarbon the heating may be carried up to 160° C. or so without explosion, but usually with the disengagement of some gas. When the material is heated to 125° C., the reaction which takes place causes the formation of considerable gas and the production of a brownish liquid of somewhat thinner consistency than polymer A. The brown liquid may be termed polymer B. This has a tendency to thicken and become quite gummy or fairly solid on exposure to air. The iodin number of polymer A, secured under these circumstances, was 35.6, while that of polymer B was 61.3.

A quantity of the crude spirit distilling up to 150° in an ordinary distilling apparatus was fractionated with a rectifying column and the following fractions were obtained:

Fractions	Percentage by volume	Iodin number
No. 1, up to 70° C.	9	310
No. 2, 70-85° C.	8.4	233
No. 3, 85-100° C.	8.6	218
No. 4, 100-115° C.	9.2	168
No. 5, 115-130° C.	8	136
No. 6, 130-150° C.	14	87.8
No. 7, above 150° C.	19	53

The color of the different fractions above tabulated varied from practically colorless in Number 1, nearly colorless in Numbers 2 and 3, slightly darker in Numbers 3 and 4, progressively to rather dark brown products in fractions 6 and 7. All the fractions ignited easily in an open dish at room temperature except fraction 7 which ignited but not as readily. When these fractions are burned in open dishes a resinous-like residue forms in some of them, the largest amount being present in fractions 2 and 3, boiling between 70 and 100° C. This resinous body is due to the presence of polymer A and may be eliminated by suitable hydrogenation, but with great difficulty by distillation.

The formation of these resinous or sticky materials in the carbureters of an internal combustion engine of course soon causes trouble. Polymer A may be converted into sulfonated or other products some of which appear to be high polymers by treatment with aqueous sulfuric or hydrochloric acid. When agitated with about 5% of sulfuric acid of 50% strength, the acid quickly turns a deep brown, but the hydrocarbon remains clear, or at the most is only tinted a yellow color. After agitation in this manner, the acid is removed by washing with water and, for example, about 5% of caustic soda solution of 20° Bé. is introduced and the hydrocarbon agitated for a time until reaction is complete; then the product is washed thoroughly with water to remove the alkali.

A quantity of this material passed through a carbureter which previously has been weighed was found to leave the carbureter free from resinous traces and any residue, if present, was negligible in amount.

The foregoing illustrates the results obtained with one sample of oil under certain conditions and, of course, considerable variations arise with changes in temperature, pressure and nature of the raw materials.

The above mentioned residue having a gravity of 38° Bé. when passed through a heated tube under approximately the same conditions, gave a yield of gasolene-like material of which 26% or thereabout was obtained by distilling up to 150° C. This is somewhat less than the percentage of gasolene-like material obtained from the first running using the original kerosene of 12° Bé. in which case over 30% of gasolene-like material distilling up to 150° C. was secured.

By the term gasolene-like material I do not wish it to be inferred that the product derived in this manner is like gasolene chemically, because ordinary or natural gasolene is either entirely saturated or shows a very slight iodin absorption. The iodin number of the raw or crude gasolene-like material obtained by this method before treatment with sulfuric acid may in some cases range around 100 to 150 and for certain fractions these may run much higher as indicated above.

Instead of using sulfuric acid under conditions to produce strict sulfonation and t- formation which takes place when the acid — highly concentrated, I preferably in accordance with the present invention use an acid which has been diluted with water or other diluting medium so that the strength is lowered, as for example to 40-60% or 70% [fol. 1168] as previously noted although this percentage may be higher or lower depending on the iodin number of the oil as well as on its other characteristics and the foregoing is merely set forth in an illustrative sense and I do not wish to be limited to any disclosure of precise procedure as laid down herein, but wish to embrace such equivalent methods of treatment or range of treatment as fall within the scope hereof.

After treating the crude product with sulfuric acid of say 50% strength, a stronger acid may follow as the more readily charred bodies may be removed by the more dilute acid and further extraction and refining by stronger acid as 60, 70 or 80% strength may then be brought about. Oxidizing agents such as a somewhat dilute solution of chromic

acid may be used to improve the color. Filtration or other suitable contact with charcoal also is useful.

The strength of the sulfuric acid to be employed in carrying out the invention in its preferred aspects may be conveniently found in a practical manner by treating a series of samples of the spirit obtained from the cracking step with acid of different strengths ranging from about 40% and upward. If a determination of the iodin number is first made to indicate the degree of unsaturation, the effect of sulfuric acid may be ascertained in one of two ways. Either the start may be made with strong concentrated acid and then progressively diluted acid used until the correct reaction strength is found. Or 40% acid may be used at the start and acid of progressively increasing strength employed until the correct reaction strength is found by this procedure. With cracked material of an iodin number of between 200 and 300 the latter method is best as the more dilute acid is likely to prove the correct reagent for permanent use. With iodin numbers below 100 the former method is recommended. If the strength of the acid is too great for desirable practical operation, especially with the products of high iodin numbers, charring or vigorous carbonization will occur and in such cases the cracked material collecting above the sulfuric acid layer after such treatment is usually discolored to such an extent as to be unsatisfactory in appearance as a commercial article while in the acid layer are frequently found carbonized masses. The acid is of a very dark or black color in most cases of this character.

With the preferred or correct strength of acid as found in this manner the reaction mass (acid) is not greatly discolored and carbonized masses are not in evidence. The upper layer of hydrocarbon is of light color and any coloration present is fairly well removed by treatment with alkali and washing. When an acid of substantially non-carbonizing or non-charring strength has thus been ascertained, such strength of acid may be regularly used in large scale operation without further examination if the plant is operated under approximately the same conditions, over an indefinite period. Of course slight variations from day to day in the cracked product do not require readjustment of conditions. Once the proper strength of acid is found for

the manner of operation in hand no change is usually required over long periods. A slightly larger or smaller proportion of olefines or other unsaturated bodies in the crude cracked spirit does not necessarily call for modification of the strength of the acid as some latitude in this respect is feasible. A light colored or water-white gasolene is prepared with difficulty from cracked oil running high in readily oxidizable olefines if too concentrated an acid is employed as some coloring matter forms which is soluble in the gasolene and which is not readily extracted by alkali and which can be removed by bleaching agents only at considerable expense. Consequently to prepare a clear water-white gasolene free from such discoloring agents, the strength of the acid may be adjusted as indicated in the foregoing so that carbonization will be so slight as not to bring about the objectionable formation of gasolene soluble dyestuffs and the adjustment of the acid to this strength for any given grade of cracked material may be made with small samples first until the desired strength of the acid is found for the particular grade of cracked material under treatment.

Ordinary natural gasolene, as stated, has a low iodin absorption or none at all while the present product has it will be noted, normally, a relatively high iodin number. In spite of this, the aforesaid treatment renders the product relatively stable. Moreover generally speaking it is more volatile than ordinary gasolene. In fact the new product having in one instance a gravity of say 52° Bé. apparently operates in carbureters equally well as or better than common gasolene of about 54° or 55° Bé. The unsaturated condition of the new product apparently renders it more reactive with oxygen enabling greater ease of ignition and more uniform explosion in internal combustion engines.

At a gravity of say 54° Bé. for both common gasolene and the preferred product of the present invention, the latter in its preferred form shows greater volatility, diffuses more easily, has a lower flash point and is ignited with greater ease and seemingly is burned more effectively than the former. It appears that a considerable degree of unsaturation is not undesirable if the gasolene has been extracted by acid of predetermined strength as above indicated, as smooth [fol. 1169] engine operation may be maintained by the use

of products of this character. The olefines, etc., which may remain after such extraction, although stable enough to be relatively permanent in storage, are yet apparently sufficiently sensitive to aid in the responsiveness of the fuel when used in internal combustion engines.

My product in its preferred aspects has an iodin number not less than 30, but preferably is higher and even may be in excess of 75 or 100, under some circumstances, and in its preferred form is substantially free from olefines readily forming resinous bodies on exposure to air.

In the accompanying drawing a cracking retort is shown with the setting in vertical section and the various condensers, conduits, stills, storage tanks, and acid treating tanks shown in vertical elevation. These drawings depict the apparatus in diagrammatic fashion for illustrative purposes.

In the drawing 1 is the setting of the cracking apparatus or retort. 2 is an inlet for oil and 3 is an inlet for water, when this is used. 4 is a coil of pipes suspended over the grate 5. 6 is an air condenser and 7 a water condenser, the outlet of the latter connects with a trap which in turn leads to the storage tank 9. 10 is a vent pipe for the gases and communicates with the gas scrubbing tower 11. 12 is an inlet pipe for the introduction of the scrubbing oil. 13 is a vent pipe for the removal of the unabsorbed gases. 14 is a storage tank for the material coming from the gas scrubbing tower having an outlet pipe 15 leading to the still 17. 16 is a pipe connecting the storage tank 9 with the still 17. 18 is a condenser, 19 a pump, and 20 is a pipe leading from the pump to the acid tank 21. A discharge pipe 22 leads from the latter to the second acid tank 23. A pipe line 24 leads from the tank 23 to a third acid tank 25. 26 is a draw-off for the finished gasolene material. 27, 28 and 29 which communicate with 30 are draw-offs for the removal of the sulfated material from the action of the sulfuric acid on the olefines of the cracked gasolene.

In the operation of this process kerosene or other suitable oil is forced into the coil 4 in which there may be a catalytic material such as fragments of nickel supported on iron, which catalytic material is not here shown. The oily material is heated in the coil to the requisite cracking temperature whereby gasolene and gases and other products

are formed and this product is passed through the air condenser and water condenser and a condensate obtained which is collected at the storage tank 9. The gases together with more or less entrained condensable material are passed into the scrubbing tower 11 and are scrubbed, the product being collected at the storage tank 14. The material in the tanks 9 and 14 is suitably distilled in the still 17 and the condensed products of a gasolene-like character are passed into the acid tank 21 where they are treated with sulfuric acid of a strength suited to the particular olefine material that is being extracted. In this tank for example, a strength of 40–60% acid may be used. The tank is fitted with an agitator which violently mixes the acid and gasolene material so that satisfactory contact with the olefines is obtained. The strength of the acid is of course preferably adjusted so that no undue charring or carbonization occurs. The gasolene material, if not sufficiently treated at this point is run into the tank 23 where it is treated with stronger acid, as for example, between 60 and 70% strength and if such treatment is not adequate to extract a sufficient amount of the olefine material the product is run into the tank 25 and treated with acid of higher strength, as for example, between 70 and 80% strength of sulfuric anhydrid. The refined gasolene is removed at the outlet 26 and may be washed with alkali in the usual manner. The various extracts of the olefine material in combination with the sulfuric acid are removed by the pipe 30.

The foregoing description is given in detail but it is to be understood that such illustrative matter is not to be construed as a limitation defining the invention in any narrower sense than is comprehended by the substance of the appended claims.

To recapitulate my process comprises the production of lighter from heavier hydrocarbons to make a product adapted for use as motor spirit, which comprises exposing the heavier hydrocarbon material to a cracking temperature as for example by passage of said material through a heated zone to effect decomposition, and in subjecting the products of such decomposition, particularly the lighter fractions, to the action of an acid comprising sulfuric acid of predetermined strength; whereby easily oxidizable olefines are extracted and in adjusting the strength of the acid

to suitably extract these and other olefine bodies which are to be removed, employing further extraction with stronger acid if required to remove olefines not extracted by the weaker acid; and my invention also embraces, as a preferred product of said process, a motor spirit consisting of or comprising cracked gasolene material, that is gasolene material made by heat decomposition of a heavier oil preferably substantially freed from olefine or kindred bodies of an easily oxidizable or resin-forming character yet containing some unsaturated bodies, and in the preferred form exhibiting an iodin absorption value or number of 30 or over, while ordinarily having a flash point lower than normal natural gasolene of corresponding specific gravity. [fol. 1170] The product of the herein described process is claimed in my copending divisional application, Serial No. 196,204, filed October 12, 1917.

What I claim is:

1. A process of producing gasolene-like material adapted for use as a motor fuel comprising subjecting a heavier hydrocarbon to a cracking temperature whereby such hydrocarbon is cracked, separating gasolene-like material from the resulting product and subjecting such gasolene-like material to the action of diluted sulfuric acid.

2. A process of producing gasolene-like material adapted for use as a motor fuel comprising subjecting a heavier hydrocarbon to a cracking temperature whereby such hydrocarbons is cracked and gasolene-like material containing a substantial amount of unsaturated bodies produced, separating gasolene-like material containing a substantial amount of unsaturated bodies from the resulting product and subjecting the separated material to the action of sulfuric acid of such strength that in its reaction with the unsaturated bodies present in the gasolene-like material a portion of such bodies are removed and no substantial and permanent discoloration of the gasolene-like material is produced.

3. A process of producing gasolene-like material adapted for use as a motor fuel comprising subjecting a heavier hydrocarbon to a cracking temperature whereby such hydrocarbon is cracked, and gasolene-like material containing a substantial amount of unsaturated bodies produced, sepa-

rating gasolene-like material containing a substantial amount of unsaturated bodies from the resulting product and subjecting the separated material to the action of diluted sulfuric acid of a strength to remove the undesirable more readily oxidizable unsaturated bodies without removing all of such unsaturated bodies.

4. A process of producing gasolene-like material adapted for use as a motor fuel comprising passing a heavier hydrocarbon through a heated zone whereby such hydrocarbon is cracked, separating gasolene-like material from the resulting product and subjecting such gasolene-like material to the action of diluted sulfuric acid.

5. A process comprising treating cracked gasolene-like material containing unsaturated bodies with diluted sulfuric acid.

6. A process comprising treating gasolene-like material containing a substantial amount of unsaturated bodies with diluted sulfuric acid of such strength that no substantial carbonization occurs.

7. A process comprising treating cracked gasolene-like materials containing unsaturated bodies with diluted sulfuric acid, the strength of the acid being proportioned with respect to the content of unsaturated bodies to remove a part and leave a part of such unsaturated bodies.

8. A process comprising treating cracked gasolene-like material having an iodin number of not less than 30 with diluted sulfuric acid whereby the iodin number is lessened but the product left with a substantial amount of unsaturated bodies.

9. A process of treating hydrocarbons comprising subjecting a hydrocarbon oil heavier than gasolene to a cracking temperature whereby a mixture of saturated and unsaturated hydrocarbons is obtained, and subjecting a portion of the products of the cracking operation consisting of saturated and unsaturated hydrocarbons, to the action of diluted sulfuric acid of such strength that initially light colored acid turns to a deep brown color upon being added to the mixture of saturated and unsaturated hydrocarbons.

10. A process of treating hydrocarbons comprising subjecting a mixture of saturated and unsaturated hydrocarbons obtained by cracking a hydrocarbon oil to successive treatment with diluted sulfuric acid whereby a substantial portion but not all of the unsaturated hydrocarbons are removed.

11. A process of treating hydrocarbons comprising subjecting a mixture of saturated and unsaturated hydrocarbons obtained by cracking a hydrocarbon oil to successive treatments with diluted sulfuric acid of different strengths, the strength of the acid employed in each treatment being such that initially light colored acid is colored a deep brown but no undue carbonization occurs upon being added to the mixture of saturated and unsaturated hydrocarbons.

Signed at Montclair, in the county of Essex and State of New Jersey, this 15th day of August, A. D. 1913.

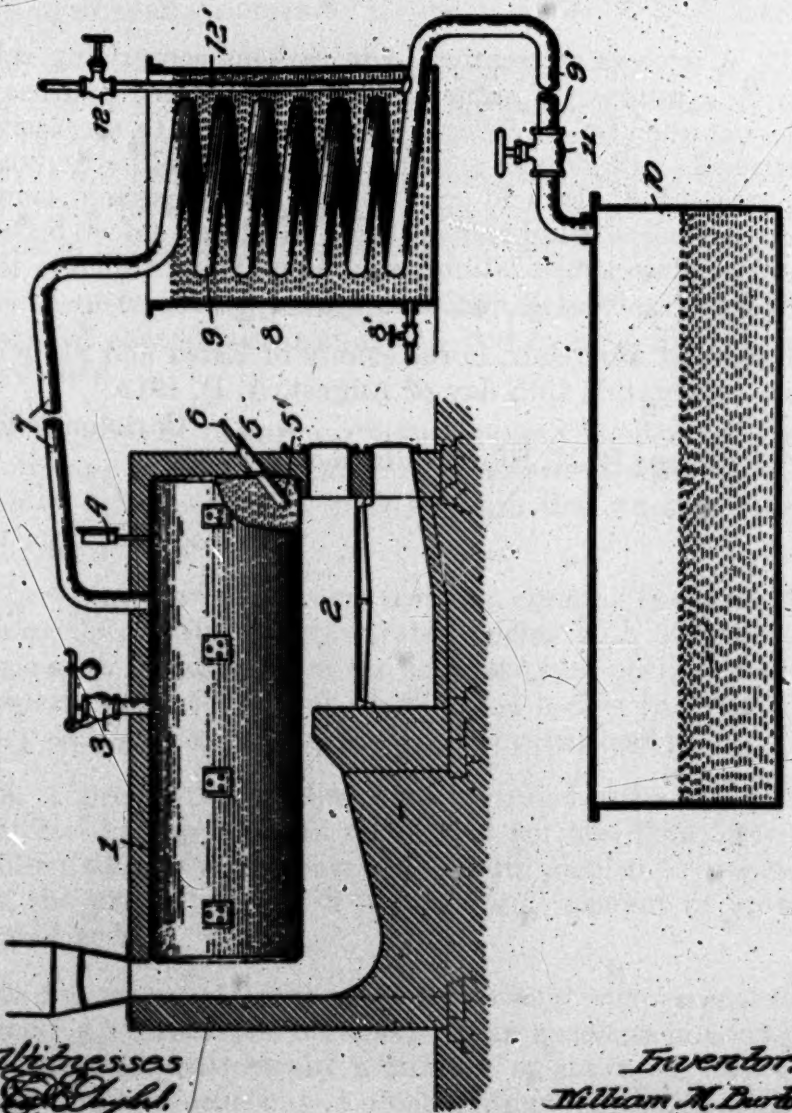
Carleton Ellis.

Witnesses: B. M. Ellis, Nathaniel L. Foster.

[fol. 1171] PETITIONER'S EXHIBIT 176

W. M. BURTON.
MANUFACTURE OF GASOLENE.
APPLICATION FILED JULY 3, 1912.

1,049,667. Patented Jan. 7, 1913.



Witnesses
E. C. Hyde.
G. F. Chase.

Inventor:
William M. Burton,
By Dyer, Hyde & Chase, Atty's.

[fol. 1172] United States Patent Office

William M. Burton, of Chicago, Illinois, Assignor to Standard Oil Company, of Whiting, Indiana, a Corporation of Indiana

Manufacture of Gasolene

1,049,667. Specification of Letters Patent. Patented Jan. 7, 1913

Application filed July 3, 1912. Serial No. 707,424

To all whom it may concern:

Be it known that I, William M. Burton, a citizen of the United States, residing at Chicago, in the county of Cook and State of Illinois, have invented a new and useful Improvement in the Manufacture of Gasolene, of which the following is a specification.

My invention relates to an improvement in the treatment of the high boiling-point residual portions, and particularly the residue of the distillation of the paraffin group or series of petroleum after the lower boiling point distillates have been removed to obtain a low boiling-point product of the same group or series.

The great and growing demand during the past ten years for gasolene has induced a large increase in the supply by improvements in the method of distilling from crude petroleum in the naphthas, the boiling points of which range from about 75° F. to 350° F. This leaves the illuminating oils, the boiling points of which range from about 350° F. to about 600° F., and the lubricating oils and waxes and, as residue, fuel-oil and gas-oil, with boiling-points ranging from about 600° F. to 700° F. The increasing demand for gasolene has induced attempts to obtain it from this residue; but these attempts, while successful in producing gasolene, have invariably, so far as I am aware, as the result of lowering the boiling point, changed the general formula of the paraffin group ($C_nH_{2n}+2$) to that of the ethylene group (C_nH_{2n}), rendering the product unmarketable because undesirable by reason of its offensive odor, for the removal of which no suitable treatment has been found.

A known method of treating the fuel and gas oils, forming the aforesaid residue of distillation of the paraffin series of petroleum, for obtaining therefrom a low-boiling-point

product involves subjecting the liquid to be treated to a temperature sufficiently high to secure so-called destructive distillation and conducting the resultant vapors through a condenser by way of a pipe or conduit connecting it with the still, but having a loaded valve interposed in the conduit between the condenser and still to maintain pressure in the latter of the vapors of distillation on the liquid. While this practice produces the desired effect of lowering the boiling point of the liquid, the condensed product, for reasons which I do not attempt to explain, is found to have been converted into distillates belonging to the objectionable ethylene group, referred to.

The object of my invention is to provide a method of treating the aforesaid residue of the paraffin group of petroleum by distillation and condensation of the vapors thereof, whereby the resultant product of low boiling-points shall be of the same paraffin series and thus free from the objection mentioned or, in other words, whereby conversion of the petroleum of that series into products belonging to the ethylene series shall be avoided. This object I accomplish by raising the boiling point of the liquid residue and increasing the heat-influence thereon while undergoing distillation by maintaining back-pressure on said liquid of the vapors arising therefrom by distillation, as has hitherto been done as aforesaid, and also maintaining the vapors themselves under pressure throughout their course from the still through the condenser and while undergoing condensation.

Suitable apparatus devised for the practise of my improvement is illustrated in the accompanying drawing by a broken view in vertical longitudinal section, diagrammatic in character, showing parts in elevation.

A boiler-like holder 1 for the liquid residue to be treated surmounts a fire-chamber 2 and is shown to be equipped with a safety-valve 3, to relieve excessive pressure in the holder, a pressure-gage 4, and a temperature-gage 5, the preferable construction of which is that illustrated of a tube 5^1 extending inclinedly into the holder through its head and closed at its inner end, for containing mercury, or by preference oil, and adapted to have withdrawably inserted into it through its outer, open end a suitable thermometer 6 for immersion into the contents of the tube under subjection to the heat in the holder. A conduit 7

leads from the top of the holder and inclines upwardly therefrom, to induce the return-flow into it of unvaporized portions of the liquid, to a condenser 8, the tank of which is shown to be provided with a lower draw-off cock 8^1. The condenser-coil 9 discharges at its lower end through a pipe-extension 9^1 thereof, of any desired length, into a receiver 10 for the products of condensation. In this pipe, and thus beyond the discharge-end of the coil, is contained a shut-off valve 11, and it is desirable to equip the coil with [fol. 1173] a relief-valve 12, shown on the upper end of a pipe 12^1 rising from near the lower end of the coil through the top of the condenser-tank, for relieving the gas-pressure which is liable to accumulate in the coil and obstruct the action of the apparatus.

The valve 11 is normally closed. From a supply of the aforesaid liquid residue contained in the holder 1, heat from the fire-chamber distills the volatile constituents, and the resultant vapors course through the conduit 7 and coil 9, wherein they are condensed. With the valve 11 tightly closed against the escape of the products of condensation, the vapors of distillation accumulate and thereafter exert a high pressure amounting from about 4 to about 5 atmospheres upon the liquid in the holder or still, raising the boiling-point from 500° F.—600° F. to 750° F.—800° F.; and this pressure of the vapors combined with their contained heat greatly enhances the conversion of the high boiling members of the paraffin series into low boiling members of the same series. The valve 11 is opened from time to time to draw off the products of condensation into the receiver 10. In fact, the intervals of drawing off should be sufficiently frequent to avoid filling the coil with liquid, for the most satisfactory operation of the apparatus. The resultant gasolene is a product belonging to the paraffin series, the same as the petroleum residue from which it was distilled. I do not herein account for the effect of the back-pressure from the extreme end of the condenser-coil upon the contents of the holder 1 in preventing transformation of the paraffin series into the objectionable ethylene series, but it is the fact that such effect ensues.

What I claim as new and desire to secure by Letters Patent is:

1. The method of treating the liquid-portions of the paraffin-series of petroleum-distillation having a boiling

point upward of 500° F. to obtain therefrom low-boiling-point products of the same series, which consists in distilling at a temperature of from about 650 to about 850° F. the volatile constituents of said liquid, conducting off and condensing said constituents, and maintaining a pressure of from about 4 to about 5 atmospheres on said liquid of said vapors throughout their course to and while undergoing condensation.

2. The method of treating the liquid-portions of the paraffin-series of petroleum-distillation having a boiling point of upward of 500° F. to obtain therefrom low-boiling-point products of the same series, which consists in distilling off at a temperature of from about 650 to about 850° F. the volatile constituents of said liquid, conducting off and condensing said constituents, maintaining a pressure of from about 4 to about 5 atmospheres on said liquid of said vapors throughout their course to and while undergoing condensation, and releasing from time to time accumulations of gas from the products of condensation.

William M. Burton.

In presence of O. C. Avisus, R. A. Schaefer.